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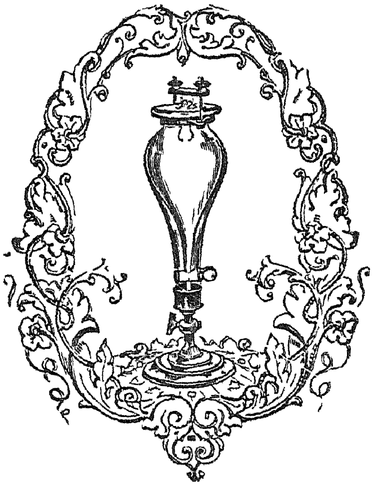

FOUNDED 1846.

HAND-BOOK

OF

CHEMISTR

BY

LEOPOLD GMELIN.

VOL. XVIII.

ORGANIC CHEMISTRY.

VOL. XII.

ORGANIC COMPOUNDS CONTAINING FROM 46 TO 96 ATOMS OF CARBON.
ANIMAL PROTEIDES, GELATINOUS SUBSTANCES, HORNY SUBSTANCES,
ANIMAL COLOURING MATTERS, VEGETABLE PROTEIDES AND
ALLIED COMPOUNDS.

TRANSLATED BY

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PREFACE

TO THE EIGHTEENTH VOLUME.

THIS volume completes the English edition of Gmelin's "Handbuch der Chemie," the first six volumes of which are devoted to Inorganic, the remaining twelve to Organic Chemistry. The original work is in seven volumes, three of Inorganic, and four of Organic Chemistry.

At Gmelin's death in 1852, the fourth and fifth volumes of the "Handbuch" (1 und 2 der Organischen Chemie, 7—11 of the Translation) were completed; and for the remainder of the work, the author had made extracts extending over the whole remaining portion of Organic Chemistry. These, however, on account of his peculiar handwriting, and the numerous abbreviations which he adopted, were very difficult to decypher; moreover, their value continually diminished as the work advanced, and in the last volume they availed but little to diminish the labour of compilation.

The continuation of the work was undertaken in 1852, by Dr. KARL LIST, now Professor of Chemistry in the Industrial School at Hagen, who wrote the first half of the sixth volume (vol. xii and vol. xiii to p. 115 of the Translation). At the beginning of 1858, the work passed into the hands of Dr. KARL KRAUT, Professor at the Polytechnic School in Hanover, who wrote the remainder of the sixth volume (vol. xiii, pp. 116—384 of Translation), and the greater part (1870 pages) of the seventh volume (vols. xiv—xviii of the Translation). The first 540 pages of the seventh volume are the work of Professors L. CARIUS, K. SCHWANERT, W. HALLWACHS, and H. RITTER.

An eighth volume has been added, treating of Physiological Chemistry, the Animal Chemistry (Zoochemie) being written by Prof. LEHMANN, the Vegetable Chemistry (Phytochemie) by Prof. ROCHLEDER. This volume, which is rather an addition to Gmelin's Handbook than an integral part of it, has not been translated. The "Zoochemie," indeed, with the exception of a few recent additions, is identical with Lehmann's "Lehrbuch der Physiologischen Chemie," a translation of which by Dr. DAY was published some years ago by the Cavendish Society.

In conclusion, I beg to tender my best thanks to several gentlemen who have assisted me in the course of the work: namely, to Mr. FRANCIS RUDALL, who translated the third, and portions of the second and fourth volumes, and made several valuable additions; to Professor G. C. FOSTER, for translation of portions of the fifteenth and sixteenth volumes, and for many valuable additions; to Professor ROBINSON, of Clifton College, for translation of the seventeenth and the greater part of the eighteenth volume; to Dr. E. ATKINSON and Dr. A. DUPRÉ for portions of the thirteenth, and to Mr. A. E. FLETCHER for part of the sixteenth volume. I have also to acknowledge the assistance of the late Mr. CHARLES E. LONG in the translation of the fourteenth volume.

HENRY WATTS.

LONDON, *September*, 1871

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COMPOUNDS CONTAINING 48 ATOMS OF CARBON.

Primary Nucleus $C^{48}H^{33}$; *Oxygen-nucleus* $C^{48}H^{36}O^2$.

Sylvinolic Acid.

$$C^{48}H^{36}O^8 = C^{48}H^{36}O^2,O^6.$$

R. Maly. *Wien. Acad. Ber.* 44, 121; *Krit. Zeitschr.* 5, 47; *J. pr. Chem.* 86, 111; *Chem. Centr.* 1862, 76; *Répert. Chim. pure* 4, 443; *Jahresber.* 1861, 389.

Formation and Preparation. When hydrochloric acid gas is passed into an alcoholic solution of abietic acid, the liquid becomes hot, and assumes a brown colour, and, after cooling, deposits sylvic acid (xvii, 318), the brown filtrate from which yields sylvinolic acid in white flocks, on addition of water.

$$C^{88}H^{64}O^{10} + 2HO = C^{40}H^{30}O^4 + C^{48}H^{36}O^8\text{?} \quad \text{(Kr.)}$$

Properties. White amorphous powder, melting at 130° with decomposition. Has an acid reaction.

	a.			*b.*		Maly. *mean.*
48 C	288	74·23	50 C	300	75·00	74·55
36 H	36	9·28	36 H	36	9·00	9·24
8 O	64	16·49	8 O	64	16·00	16·21
$C^{48}H^{36}O^8$	388	100·00	$C^{50}H^{36}O^8$	400	100·00	100·00

Maly gives the formula *b*, but the formation of sylvinolic acid from abietic acid seems to support the formula with 48 atoms of carbon.

Sylvinolic acid is insoluble in *water*. — It is *bibasic*, and forms neutral salts having the formula $C^{48}H^{34}M^2O^8$.

Potash and Soda salts. — Amorphous masses, soluble in alcohol, and forming opalescent liquids in water.

Lime-salt. — Obtained by precipitating an alcoholic solution of the acid with alcoholic chloride of calcium and ammonia. Bulky flocks, slightly soluble in alcohol.

	Flocks.		Maly.
$C^{48}H^{34}O^6$	370	86·85	
2 CaO	56	13·15	10·24
$C^{48}H^{34}Ca^2O^8$	426	100·00	

Silver-salt. — Nitrate of silver throws down from the alcoholic acid a white powder, which reddens on exposure to light, and dissolves easily in ammonia-water, and with difficulty in alcohol.

			Maly.
$C^{48}H^{34}O^{6}$	370	61·46	
2 AgO	232	38 54	37·04
$C^{48}H^{34}Ag^{2}O^{8}$	602	100·00	

Sylvinolic acid dissolves easily in *alcohol* and in *ether*, and is left behind in the form of a pitch on evaporating the solution.

Conjugated Compounds of Sylvinolic Acid.

1. Summary of the Constituents of the Pine resins.

The resinous sap which exudes from various species of conifers, contains a volatile oil (xiv, 240) and one or more non-volatile constituents, which consequently are found in turpentine, as well as in the colophony or resin obtained by distilling turpentine with water and melting the residual mass.

a. According to Unverdorben, colophony is to be regarded as impure (amorphous) pinic acid. Turpentine, French colophony, and the resin of *Pinus sylvestris*, contain also (crystallisable) sylvic acid, together with smaller portions of other resins. Trommsdorff, Rose, and Liebig likewise distinguish pinic and sylvic acids as two different acids.

b. According to Laurent, the turpentine of *Pinus maritima*, as well as the other species of pine, contains (crystallisable) pimaric acid, which is converted on standing into the isomeric pinic acid (formerly described as amorphous pimaric acid), and by distillation into the likewise isomeric sylvic acid (formerly distinguished as pyromaric acid). Strecker (*Ann. Pharm.* 68, 338) regards sylvic, pimaric, and pyromaric acids as identical, whilst according to Sievert, sylvic and pimaric acids are different; the latter, however, volatilises unaltered, so that Sievert regards Laurent's pyromaric acid as pimaric acid.

c. According to Maly, whose view is here regarded as the soundest, colophony or pinic acid is the anhydride of abietic acid, and susceptible of conversion into (crystallised) abietic acid by absorption of water. The salts of pinic acid are formed from abietic acid, by the absorption of water. The sylvic acid of Unverdorben is also abietic acid; but not that of Sievert, who decomposed abietic acid by the action of sulphuric acid, and examined the body thus formed as sylvic acid, $C^{40}H^{30}O^{4}$ (xvii, 318).— If the latter part of Maly's view is well founded, Trommsdorff, Rose, and Liebig must have examined sylvic acid, whilst it is not clear from the statements of Unverdorben and Sievert, whether they refer to the acid prepared with sulphuric acid, or to that obtained by crystallisation (Kr).— Maly is inclined to regard Laurent's pimaric acid also as abietic acid.

2. Abietic Acid.

$$C^{88}H^{64}O^{10} = C^{48}H^{34}O^{6},C^{40}H^{30}O^{4}.$$

MALY. *Wien. Akad. Ber.* 44, 121; *Krit. Zeitschr.* 5, 47; *J. pr. Chem.* 86, 111; *Chem. Centr.* 1862, 73; *Rép. Chim. pure*, 4, 443; *Kopp's Jahresber.* 1861, 389.— *Ann. Pharm.* 129, 94; *J. pr. Chem.* 92, 1;

Chem. Centr. 1864, 508; *Krit. Zeitschr.* 7, 441; *Kopp's Jahresb.* 1863, 402. — *Ann. Pharm.* 132, 249; *Kopp's Jahresb.* 1864, 408. — *J. pr. Chem.* 96, 145; *Chem. Centr.* 1865, 1160; *Kopp's Jahresb.* 1865, 402.

See other researches under sylvic acid (xvii, 318). — *Abietinsäure* (Maly) to be distinguished from the abietinic acid of Caillot.

Source. As abietic anhydride it forms, together with volatile oil the chief constituent of the resin of *Pinus Abies*, *P. Larix*, and probably of other pines and firs.

Preparation. Powdered colophony is digested for a week with 70 per cent. alcohol, whereby it is converted into a granular mass; the liquid is separated; and the residue is dissolved in alcohol of 90 to 92 per cent., then filtered, and completely precipitated by mixing the solution with hot water. After pouring away the liquid, the brown resinous cake is converted, on standing for 1 to 3 weeks, into a crystalline mass, enclosing in its interstices a brown soft resin. The latter body is removed by cold alcohol, and the crystals are pressed and purified by crystallisation from hot alcohol. In this way crystals are obtained amounting to 80 p. c. of the colophony employed (Maly).

Properties. Irregular, transparent, pointed crystals grown together by their broader ends, or white, pointed, oval laminæ (Maly). Doubly oblique prismatic? There are five faces (fig. 70); *u'* before and behind, *t* before and behind to the left, and *p*. — Angle *t* behind : *u'* behind = 47°; *t* before : *u* before = 131° 30'; *p* : *u'* = 69°; *t* behind : *p* = 104° (by calculation 104° 35'); *t* before : *p* = 133° 30' (v. Lang, *J. pr. Chem.* 96, 162). — When heated to above 100° for some time, it cakes together slightly. It begins to melt at 129°, and melts completely at 144° without losing weight. Has an acid reaction. It is eliminated by the kidneys unaltered.

				Maly.	
	Crystals.			*mean.*	(Kraut.)
88 C	528	78·57	78·63	78·54	78·37
64 H	64	9·52	9·80	9·65	9·68
10 O	80	11·91	11·57	11·81	11·95
$C^{88}H^{64}O^{10}$	672	100·00	100·00	100 00	100·00

¶ Strecker (*Ann. Pharm.* 150, 131; *Zeitschr f. Chem.* [2], 6, 381) denies the existence of Maly's abietic acid, and regards the formula $C^{88}H^{64}O^{10}$ as founded on incorrect analyses. He points out that the so-called abietic acid is prepared from the same material, and in the same manner, as the sylvic acid of Unverdorben, Trommsdorff, Siewert, and others (xvii, 318), Trommsdorff and Siewert in particular, not having used sulphuric acid in the preparation, by which, according to Maly, abietic acid undergoes a transformation; moreover, that the properties of abietic acid, as described by Maly, exhibit a general agreement with those of sylvic acid, excepting in the melting point, which has been stated by various authors at temperatures ranging between 129° and 162°; Duvernoy found 129°; Maly's own statements, made at different times, vary between 129° and 165°. For these reasons Strecker regards abietic acid as identical with sylvic acid, and as having the composition $C^{40}H^{30}O^4$. The same view is held by Duvernoy (*Ann. Pharm.* 148, 143; *Zeitschr f. Chem.* [2], 5, 303). See on the contrary Maly (*Ann. Pharm.* 149, 244; *Zeitschr f. Chem.* [2], 5, 304) ¶.

Decomposition. 1. On passing *hydrochloric acid gas* into alcoholic abietic acid, sylvic (xvii, 318,) and sylvinolic acids are formed:

$$C^{88}H^{64}O^{10} + 2HO = C^{48}H^{36}O^{8} + C^{40}H^{30}O^{4}? \quad \text{(Kr.)}$$

When abietic acid is added to boiling alcoholic hydrochloric acid, and distilled, a small quantity of oily drops, probably of an ethyl-compound, passes over. — 2. Abietic acid is but little altered in appearance by dry *chlorine*, but it evolves hydrochloric acid gas, and increases about 14·13 p. c. in weight.

The product is Maly's *dichlorabietic acid*, $C^{44}Cl^{2}H^{30}O^{5}$, in accordance with his older formula for abietic acid, $C^{44}H^{32}O^{5}$. In the formation of this body, however, 100 parts of abietic acid must have taken up 20·53 parts, and not as Maly calculates, 13·4 parts, of chlorine. The statement that this acid contains 16·92 p. c. of chlorine (calc. 17·53 p. c. Cl) is in favour of Maly's formula $C^{44}Cl^{2}H^{30}O^{5}$, or $C^{88}Cl^{4}H^{60}O^{10}$; but this formula is inconsistent with the fact that the soda-salt of the acid contains 10·45 p. c. of soda, whilst by calculation it should contain only 7·26 p. c. (Kr.). — "Dichlorabietic acid" forms a whitish-yellow mass of acid reaction, melting at 124°, with liberation of suffocating vapours. It dissolves less freely than abietic acid in hot dilute caustic soda, and is precipitated unaltered by acids. It is less soluble than abietic acid in alcohol, easily soluble in ether. Its soda-salt, obtained by adding carbonate of soda to a hot alcoholic solution of the acid and evaporating, forms an alkaline brittle resin.

3. Abietic acid dissolves easily when triturated with *oil of vitriol*, forming a reddish-brown solution, from which it is at first precipitated by water unchanged. When the solution is slightly warmed, or allowed to stand for 24 hours, it evolves sulphurous acid, after which water throws down a reddish precipitate containing sulphur, which dries up to a whitish-yellow mass over oil of vitriol. This body is decomposed at the temperature of 80° in the moist state, with liberation of sulphuric acid, and even when dry it turns soft and blackens below 100°. It has an acid reaction; forms with alkalis uncrystallisable compounds, and with baryta a compound which is insoluble in alcohol, and contains sylvic acid, together with about an equal number of atoms of sulphuric acid. It dissolves slightly in alcohol, and very easily in ether-alcohol, forming a purplish-violet solution, which turns brown on standing — On mixing a hot alcoholic solution of abietic acid with sulphuric acid, sylvic acid is produced. No sugar is formed, even after long standing.

4. When triturated with *pentachloride of phosphorus*, abietic acid turns warm and brown and becomes fluid; the product yields on distillation, hydrochloric and chlorophosphoric acids in succession, and, lastly, at 295° to 350°, and still higher temperatures, a volatile oil, whilst charcoal remains behind (Maly).

The volatile oil, Maly's *abietone*, forms when rectified a wine-yellow fluorescent liquid, of faint aromatic odour, free from chlorine, and when rectified over sodium, free from oxygen. It solidifies to an amorphous mass in the cold. When it is submitted to fractional distillation and collected in four portions, the separate portions, the first of which distils at 295° to 303°, have the composition given below, for which Maly gives the accompanying formulæ. *Bromabietone*, obtained by dissolving the first portion in ether and adding bromine, is dark-brown, not decolorised by potash, and contains 23·6 to 27·2 p. c. of bromine.

	a.	Maly.		*b.*	Maly.
88 C	89·80	89·84	88 C	90·41	90·24
60 H	10·20	10·21	56 H	9·59	9·50
$C^{88}H^{60}$	100·00	100·05	$C^{88}H^{56}$	100·00	99·74

	c.	Maly.		d.	Maly.
88 C	90·72	90·40	88 C	91·35	91·12
54 H	9·28	9·19	50 H	8 65	8·79
$C^{88}H^{54}$	100 00	99·59	$C^{88}H^{50}$	100·00	99·91

5. Abietic acid is converted by the action of *sodium-amalgam* into hydrabietic acid. — 6. When fused with *hydrate of potash* it yields propionic, but no protocatechuic acid (Maly).

Combinations. Abietic acid is *bibasic*, and forms (rarely) *acid* and (generally) *neutral* salts.

Ammonia-salt. — Abietic acid dissolves easily in alcoholic ammonia. In aqueous ammonia the crystals swell up, turn cloudy, and dissolve, at first to an opalescent liquid, which becomes clear on warming or on addition of more ammonia. The solution solidifies to a clear stiff jelly on cooling.

Abietic acid dissolves in warm *potash* and *soda-ley*, without forming crystallisable compounds. These solutions, and that obtained by adding carbonate of soda to the alcoholic acid, dry up to yellow amorphous brittle masses, soluble in alcohol. — The acid is not soluble in aqueous carbonate of potash.

Baryta-salt. — Chloride of barium throws down from the aqueous potash-salt dense flocks, which dissolve more easily in alcohol than in water.

			Maly.
$C^{84}H^{62}O^{10}$	670	83·02	
2 Ba	137	16·98	17·11
$C^{88}H^{62}Ba^2O^{10}$	807	100·00	

Lime-salt. — Formed by mixing an alcoholic solution of the ammonia-salt with alcoholic chloride of calcium. A portion of the compound is precipitated at once, and the greater part on pouring the filtrate into a large quantity of water. — White powder, which does not lose weight at 100°. Dissolves easily in alcohol, slightly in water.

$C^{88}H^{62}O^{10}$	670	94·37	
2 Ca	40	5·63	5·80
$C^{88}H^{62}Ca^2O^{10}$	710	100·00	

An *acid lime-salt* cannot be obtained in the same way as the corresponding magnesia-salt (Maly).

Magnesia-salt. — A. *Neutral.* — Aqueous chloride of magnesium forms with the potash-salt, flocks which change to a dense sandy deposit. — The salt dissolves with difficulty in water, and easily in alcohol.

Over oil of vitriol.			Maly. *mean.*
	670	96·53	
	24	3·47	3·53
	694	100·10	

B. *Acid.* — Obtained by boiling alcoholic abietic acid with carbonate of magnesia as long as a test-portion of the liquid is turned milky by water, and until a flocculent precipitate is formed; filtering into a large quantity of water; and collecting the quickly deposited flocks. — Light, white mass, resembling magnesia. Becomes electric when rubbed, and hardens at 100°, without losing weight. — Dissolves easily in alcohol, and is precipitated from the solution by water.

			Maly.	(Kraut.)
$C^{88}H^{63}O^{10}$	671	98·25		
Mg	12	1·75	1·56	1·62
$C^{88}H^{63}MgO^{10}$	683	100·00		

Alumina-salt. — White flocks, slightly soluble in water and in alcohol, easily soluble in ether and in bisulphide of carbon.

Zinc-salt. — Formed from the potash-salt and sulphate of zinc. — White flocks, nearly insoluble in water, slightly soluble in alcohol, and freely in ether.

	Over oil of vitriol.		Maly. *mean.*
$C^{88}H^{62}O^{10}$	670	91·15	
2 Zn	65	8·85	9·13
$C^{88}H^{62}Zn^{2}O^{10}$	735	100·00	

The potash-salt throws down from *nitrate of cobalt* a peach-blossom coloured, and from *mercurous nitrate*, a white precipitate, both unchanged by boiling.

Copper-salt. — A solution of abietic acid in ether or bisulphide of carbon, takes up a large quantity of oxide or carbonate of copper. — Sulphate of copper throws down from the potash-salt of abietic acid pale-green flocks, slightly soluble in water and alcohol, easily soluble in bisulphide of carbon and ether, with splendid green colour.

			Maly.
$C^{88}H^{62}O^{10}$	670	91·36	
2 Cu	63·6	8·64	8·67
$C^{88}H^{62}Cu^{2}O^{10}$	733·6	100·00	

Silver-salt. — Alcoholic nitrate of silver throws down from a warm alcoholic solution of abietic acid, on addition of a drop of ammonia-water, a white pulverulent precipitate, slightly soluble in alcohol and very easily soluble in ammonia-water and ether. This salt alone, and no acid salt, is formed also when an ethereal solution of the silver-salt is mixed with excess of abietic acid and precipitated by ammonia, or when the acid magnesia-salt is precipitated by nitrate of silver.

			Maly.
88 C	528	59·61	59·51
62 H	62	6·99	7·39
10 O	80	9·03	9·07
2 Ag	216	24·37	24·03
$C^{88}H^{62}Ag^{2}O^{10}$	886	100·00	100·00

Five other salts contained 25·71 to 26·32 p. c. of oxide of silver (theory requires 26·17 p. c. AgO).

Abietic acid is soluble in *bisulphide of carbon*, *wood-spirit*, *chloroform*, *ether*, and *benzene* (Maly). It does not combine with *urea* or *aniline* (Maly).

3. Abietate of Ethyl.

$$C^{96}H^{72}O^{10} = 2C^4H^5O,C^{88}H^{62}O^8.$$

R. Maly. *J. pr. Chem.* 96, 145.

Freshly precipitated abietate of silver is added, in small portions, to iodide of ethyl previously diluted with ether, whereupon the mixture becomes warm and iodide of silver separates. After standing for 24 hours, the liquid is filtered, and the filtrate evaporated over the water-bath. The product is purified by dissolving it in ether-alcohol, precipitating with water, taking up the oily drops which separate with ether, and evaporating. — This body is not formed by passing hydrochloric acid gas into alcoholic abietic acid, and is only sparingly formed by distilling an alcoholic solution of abietic acid with oil of vitriol.

Abietate of ethyl forms a yellowish, clear, somewhat soft mass, of a syrupy consistence at 100° and having a resinous ethereal odour. — It is decomposed by distillation, with elimination of water. — It is insoluble in *water*, but sparingly soluble in *alcohol*, easily in *ether* and *ether-alcohol*.

			mean.
96 C	576	78·15	78·16
73 H	73	9·90	9·92
11 O	88	11·95	11·92
$2C^4H^5O,C^{88}H^{62}O^8 + HO$	737	100·00	100·00

The formula $2C^4H^5O, C^{88}H^{62}O^8$ requires 79·1 p. c. C., 9·69 H.

4. Abietin.

$$? \; C^{106}H^{76}O^{16} = 3C^6H^5O^3,C^{88}H^{61}O^7.$$

R. Maly. *J. pr. Chem.* 96, 146.

A mixture of concentrated alcoholic abietic acid and glycerin, after standing for 14 days in the cold, deposits small white crystals, which after washing with water melt at 125°, and dissolve in ether and alcohol, but cannot be recovered from the solutions in an unchanged state. The crystals are formed from 3 atoms of glycerin and 1 atom of abietic acid, with elimination of 12 atoms of water:

$$C^{88}H^{64}O^{10} + 3C^6H^8O^6 = 3C^6H^5O^3,C^{88}H^{61}O^7 + 12HO.$$

			Maly.
106 C	636	75·71	75·38
76 H	76	9·04	9·23
16 O	128	15·25	15·39
$3C^6H^5O^3,C^{88}H^{61}O^7$	840	100·00	100·00

5. Abietic Anhydride.

$C^{88}H^{62}O^{8} = C^{48}H^{33}O^{5},C^{40}H^{29}O^{3}$.

MALY. *Ann. Pharm.* 132, 249; *J. pr. Chem.* 96, 140.

Abietic acid does not undergo any alteration at 100°, and even at higher temperatures does not give off water until it begins to be coloured and decomposed. Neither does it yield an anhydride when melted in a stream of carbonic acid and more strongly heated.—But the formation of abietic acid from pine and larch resins, as well as from colophony, is the result of the absorption of water, so that these bodies must be regarded as the anhydride of abietic acid, or as mixtures containing it, as the following experiments show:

a. Colophony dried over oil of vitriol is dissolved in alcohol; and water is added to the solution till turbidity is produced; then after the formation of a mass of crystals of abietic acid, the whole is evaporated, and the residue is again dried over oil of vitriol, and lastly in the water-bath. In this way 96·5 parts of colophony take up 3·5 parts of water, corresponding to the formula $C^{88}H^{62}O^{8} + 2HO$ (calc. 3·82 parts HO).

b. A solution of colophony in absolute alcohol deposits no crystals, even after standing for months, whereas a solution in alcohol of 70 p. c. deposits as much as 80 p. c. of the amount dissolved in 8 days.—Similarly the resinous drops which exude from pine trunks retain their transparency, after becoming hard from loss of volatile oil, and turn milky and crystalline only in wet weather.

c. When the resin collected from pines or larches is freed from volatile oil over the water-bath, there remains an amorphous yellow residue, which softens between 90° and 100°, is of a syrupy consistence at 100°, and dissolves easily in alcohol, ether, and chloroform. This body has the composition of abietic anhydride.

			Maly. *Pine and Larch resins.*
88 C	528	80·73	80·23
62 H	62	9·48	9·87
8 O	64	9·79	9·90
	654	100·00	100·00

6. Hydrabietic Acid.

$C^{88}H^{68}O^{10} = C^{88}H^{68}O^{4},O^{6}$.

MALY. *J. pr. Chem.* 96, 149.

Sodium-amalgam is added to a warm alcoholic solution of abietic acid so long as each fresh addition continues to produce a perceptible action, and the resulting soda-salt is allowed to crystallise in the cold. From the aqueous solution of this salt, neutral acetate of lead throws down hydrabietate of lead, which is decomposed under alcohol by hydrosulphuric acid. The solution, freed from sulphide of lead by filtration, yields crystals of hydrabietic acid on spontaneous evaporation.

White fatty laminæ, melting partially at 140° and completely at 160°. — Burns on platinum foil, evolving resinous vapours, and leaving no residue.

			Maly. *mean.*
88 C	528	78·10	77·97
68 H	68	10·05	10·28
10 O	80	11·85	11·75
$C^{88}H^{68}O^{10}$	676	100·00	100·00

Hydrabietic acid is insoluble in *water*. — It is *bibasic*, and forms neutral salts, represented by the formula, $C^{88}H^{66}M^{2}O^{10}$.

Soda-salt. Long, silky needles, which effloresce rapidly in the air, and lose the whole of their water at 100°.

			Maly.
$C^{88}H^{66}O^{10}$	674	87·08	
2 Na	46	5·94	6·18
6 HO	54	6·98	6·62
$C^{88}H^{66}Na^{2}O^{10} + 6HO$	774	100·00	

Lime-salt. Precipitated by chloride of calcium from the ammonia-salt, in white flocks soluble in alcohol.

The aqueous soda-salt produces white precipitates with *neutral acetate of lead*, *mercurous nitrate*, and *nitrate of silver;* it does not precipitate *mercuric chloride.*

Hydrabietic acid dissolves easily in *alcohol* and *ether.*

Appendix to Abietic Acid.

1. Colophony and Pinic Acid.

The colophony or resin, obtained by distilling turpentine with water and melting the residual mass, is to be regarded, according to Unverdorben, as impure pinic acid, or according to Maly, as abietic anhydride. Pinic acid occurs also in white resin and in turpentine.

Unverdorben's pinic acid is obtained by distilling Venice turpentine with water, so that the oil of turpentine passes over; dissolving the residue in 65 p. c. alcohol; precipitating the solution with alcoholic acetate of copper; washing the precipitate with absolute alcohol; dissolving it in alcohol containing hydrochloric acid, and mixing the solution with ⅛th of its volume of water. — It forms a colourless transparent mass, hard and brittle in the cold, but elastic when warmed, and melting like colophony. It is inodorous, and has a very faintly bitter taste (Unverdorben). Sp. gr. of colophony = 1·0727 (Brisson), 1·08 (Thomson). Pinic acid is obtained by the spontaneous evaporation of its ethereal solutions in amorphous granules containing 77·66 p. c. C., 9·73 H., and 12·61 O., and is consequently isomeric with sylvic acid (Laurent, *Ann. Chim. Phys.* 65, 324).

According to Unverdorben, colophony (as also the resin of *Pinus* *sylvestris*) contains two other resins, differing from the preceding: *a.* A resin soluble in rock-oil and oil of turpentine, obtained by digesting colophony or pine-resin with carbonate of magnesia, boiling the filtrate with water, separating the precipitate thereby formed, evaporating the solution to dryness, exhausting the residue with water, and precipitating the solution with acids. — *b.* A resin easily soluble in aqueous ammonia and in weak spirit, but insoluble in ether and rock-oil, obtained by distilling with water a solution of 7 parts of colophony in 6 parts of alcohol, whereby a resin is deposited, and adding phosphoric acid to the solution.

Colophony remains almost unaltered, even after prolonged fusion; it turns brown slowly, but scarcely loses weight when kept for some days, at the temperature of 140—150° (Maly). The brown decomposition-product formed on boiling is Unverdorben's *colopholic acid.* — When colophony is heated to a temperature of 200° to 400°, and subjected to a current of superheated steam, it is volatilised, apparently without decomposition. The distillate forms, after dehydration, a colourless, perfectly transparent, glassy mass, in which stellate groups of crystals appear after very long standing (Hunt & Pochin's patent, *Hann. Gewerb. Mittheil.* 1859, 318). Weidenbusch's objections to this process (*Krit. Zeitschr.* 1860, 263) are founded on totally erroneous conceptions. Colophony thus distilled yields abietic acid by Maly's process (Kr.).

Pinic acid subjected to dry distillation yields hydrocarbons, tar, water containing acetic acid, colopholic acid, and a large quantity of unchanged pinic acid. In the distillation of large quantities, more water, and instead of tar a brownish-yellow oil, and very little pinic acid pass over (Unverdorben). — The rapidly conducted dry distillation of colophony yields water, a carbonaceous residue, and an oily distillate, which contains colophene (xiv, 279) together with undecomposed colophony, and cannot be quite freed from dissolved colophony by repeated distillation. There is also formed an oil isomeric with colophene, having no action on polarised light, probably terebene (xiv, 273), (Deville, *Ann. Chim. Phys.* 75, 69).

When commercial pine-resin is kept in a state of fusion so long as it continues to give off water and turpentine, and until it begins to decompose, and is then submitted to dry distillation, it yields water and Frémy's *resinein.* The latter body forms, after rectification, a faintly coloured, very dense, nearly inodorous and tasteless liquid, boiling at 250°. It is resinised by nitric acid and by litharge, with separation of lead; it burns like fat oils, but with more smoke; is insoluble in potash-ley, but slightly soluble in alcohol and easily in ether. Resinein contains 84·1 p. c. C., 10·7 H., and 5·2 O., corresponding to the formula $C^{40}H^{30}O^{2}$ (Frémy).

Colophony intimately mixed with 8 parts of lime, and distilled at a gradually increasing temperature, yields a mixture of volatile oils having an ethereal odour, together with a little water. The mixture yields by rectification the following bodies:—

a. *Resinone*, melting at 78°, colourless, limpid, of burning taste, and inflammable like alcohol. It is insoluble in water, but dissolves in alcohol (whereby a little oil of turpentine is separated) and in ether. It contains 78·44 p. c. C., 11·60 H., and 9·96 O., corresponding to the formula $C^{20}H^{18}O^{2}$ (Frémy).

b. *Resineone*, melting at 148°, a less limpid oil of less burning taste than *a*, and not so freely soluble in alcohol. It contains 83·92 p. c. C., 11·20 H., and 4·88 O., and is represented by the formula $C^{29}H^{23}O$ (Frémy, *Ann. Chim. Phys.* 59, 13 ; *Ann. Pharm.* 15, 284).

When melted pine-resin is allowed to drop upon coke heated to redness in iron cylinders, as in the manufacture of resin-gas, liquid and gaseous products are evolved, whilst carbon is left behind. The liquid products amount to $\frac{3}{10}$ths of the resin employed. When submitted to fractional distillation, they yield, at 130° to 160°, a limpid oil, afterwards, at 280° to 350°, a thick oil, and at intervening temperatures naphthalin ; above 350° there passes over a body which solidifies in the condenser, whilst charcoal is left behind.

The limpid oil, treated according to xii, 227, and xiii, 339, yields toluol and cumol: the solid body contains metanaphthalin (xiv, 10). These substances, as well as naphthalin, are contained also in the thick oil, from which however an oil boiling at 238° may be separated by repeated fractional distillation, or by treatment with oil of vitriol and caustic potash. This oil, Pelletier and Walter's *retinol*, is colourless, inodorous and tasteless, and resembles a fat oil; its sp. gr. is 0·9, and its vapour-density 7·11. It contains on the average 91·19 p. c. C. and 7·94 H., and agrees with the formula $C^{32}H^{16}$ (calc. 92·31 p. c. C., 7·69 H. ; vapour-density 7·21), (Pelletier & Walter, *Ann. Chim. Phys.* 67, 299 ; *J. pr. Chem.* 14, 214).

The gas evolved during the dry distillation of colophony in cast-iron retorts contains, about the middle of the distillation, carbonic acid, carbonic oxide, ethylene, butylene, and towards the end of the operation a larger proportion of carbonic acid, together with marsh-gas; on cooling, it deposits also a volatile oil. The liquid products of distillation are at first a yellow limpid oil (essence of resin, *vive essence, Harzessenz*), and afterwards, at higher temperatures, thick fluorescent *resin-oil* (*huile de resine*).

The essence of resin yields by oft-repeated fractional distillation a product boiling at 97°, and another boiling at 160°. The former, Schiel's *colophonone*, is colourless, limpid, highly refractive, and of sp. gr. 0·84 at 14°. It mixes with oil of vitriol, forming a brown liquid from which water separates a green oil. Nitric acid converts it into a resin. It turns brown when heated above its melting-point, and also when acted upon by potassium, in the latter case with brisk evolution of gas. It does not rotate a ray of polarised light. Vapour density about 5·1. It contains, on the average, 79·12 p. c. C., 11·74 H., and 9·14 O., corresponding to the formula $C^{22}H^{18}O^{2}$ (by calc. 79·52 C., 18·85 H.). — The oil boiling at 160° is greenish-yellow, without action on polarised light, and contains 87·44 p. c. C., and 11·78 H., and is therefore isomeric if not identical with terebene (xiv, 273).

The resin-oil contains 86·28 p. c. C., 9·95 H., and 2·77 O., corresponding to the formula $C^{60}H^{40}O^{2}$ (calc. 86·44 C., 9·62 H.). After being heated for 24 hours with lime it is no longer fluorescent, and contains when rectified 84·70 p. c. C., 9·69 H., and 5·61 O., agreeing in composition with Deville & Frémy's resinein (the formula $C^{40}H^{28}O^{2}$ requires 84·51 p. c. C., and 9·80 H.) (Schiel, *Ann. Pharm.* 115, 96). — See also Lonyet (*Compt. rend.* 26, 183).

Colophony is decomposed by distillation with *nitric acid*. — It absorbs *sulphurous acid gas*, which is liberated on dissolving in alcohol. — It dissolves in cold *oil of vitriol* without elimination of sulphurous acid, and is precipitated from the solution by water; fuming sulphuric acid carbonises it (Unverdorben). — *Potassium* and *sodium* undergo oxidation slowly in melted colophony, without evolution of light (Gay-Lussac & Thénard). — Pinic acid dissolved in alcohol and exposed to the air is converted into two resins, one of which, by much the greater part, is insoluble in rock-oil. This resin is formed also when pinic acid in combination with aqueous alkali is exposed to the air (Unverdorben).

The flocculent colophony obtained by precipitating an alkaline solution with hydrochloric acid contains, after drying in the air, 13·1 p. c. of *water*. Colophony also takes up a little water when boiled therewith, becoming at the same time opaque and brittle (Unverdorben).

Pinic acid combines with *bases* to form salts. Excess of pinic acid expels carbonic acid from aqueous carbonates of the alkalis on boiling. Dry carbonate of potash is slowly dissolved by an ethereal, and still more slowly by an alcoholic solution of pinic acid, but is rapidly dissolved by a solution in oil of turpentine. The fused acid also expels carbonic acid from the carbonates of potash, soda, lime, and magnesia, and decomposes chloride of calcium, chloride of magnesium, and succinate and benzoate of potash. Alcoholic pinic acid precipitates alcoholic solutions of acetates, forming pinates. — Salts of pinic acid are obtained (1) by dissolving the acid in an aqueous solution of the base; (2) by precipitating the alcoholic solution of an acetate with alcoholic pinic acid, dissolving the precipitate in ether, and precipitating with alcohol, which retains in solution the excess of pinic acid; (3) by double decomposition. — The salts are amorphous, partly pulverulent, partly resinous. Their solutions are decomposed by acetic, boracic, and stronger acids. — A few only dissolve in water and alcohol, but all in ether, and the greater number in excess of pinic acid (Unverdorben).

Pinate of Ammonia. — Powdered colophony absorbs 3·02 p. c. of ammonia-gas in an hour, and no more afterwards (1 atom of NH^3 to $C^{88}H^{62}O^8 = 2·6$ p. c.). The compound gives off the greater part of the ammonia in the air, and dissolves to a very slight extent in water, leaving a sticky mass. — A solution of pinic acid in aqueous ammonia becomes thick and turbid on cooling; when boiled, it gives off ammonia and deposits pinic acid.

Pinate of Potash. — On boiling an ethereal solution of pinic acid with carbonate of potash a colourless mass is obtained. — Hot, very dilute potash-ley takes up colophony in all proportions, and forms a thick liquid, cooling to a viscid mass, from which water extracts a little potash-salt. On saturating hot potash-ley with colophony, evaporating the brownish-yellow solution, and drying the residue at 100°, the colophony is found to have taken up from concentrated solution of potash 9·9, and from diluted solution 17·5 p. c. of potash. The compound dissolves slowly in all proportions of water, forming a solution which, when it contains ⅕th of the salt, is oily and of sp. gr. 1·042, and from which caustic potash, carbonate, and acetate of potash, chloride of sodium, sulphate of soda, and other salts precipitate a semi-fluid mass. — The salt dissolves in alcohol and ether, but not in oil of turpentine, or olive oil (Unverdorben).

The *soda-salt* contains 7·6 parts of soda to 100 parts of colophony. — The *baryta-salt* is a yellowish-white powder, containing 13 parts of baryta to 100 of colophony; it is insoluble in alcohol, but easily soluble in ether. — The *lime-salt*, obtained by double decomposition, contains

5·17 parts of lime to 100 of colophony; it dissolves easily in ether and oil of turpentine.—The *magnesia-salt*, precipitated from sulphate of magnesia by pinate of potash, contains 3·7 parts of magnesia to 100 of colophony; it dissolves easily in ether, but not in alcohol.

Pinate of Zinc.—Pinate of potash throws down from solutions of zinc sulphate yellowish-brown flocks, which, when precipitated from concentrated solutions, contain 7 parts, and from dilute solutions 10 to 11 parts of zinc oxide to 100 parts of colophony. The compound is insoluble in alcohol, but completely soluble in ether and in boiling linseed oil; it dissolves also in oil of turpentine, with separation of flocks.—When zinc-oxide is heated to 300°, with a little pinic acid, the mass takes fire and smoulders (Unverdorben).

Pinate of Lead.—White, very soft powder, not sticky at 100°, but fusible to a transparent resin at a higher temperature. It dissolves in oil of turpentine and fat oil, and very slightly in alcohol and ether.—The salt precipitated by alcoholic pinic acid from an alcoholic solution of neutral acetate of lead contains 13 to 15 p. c. (Unverdorben), 27·31 p. c. (Rose), 25 p. c. (Pelletier) of lead oxide.

Ferrous pinate is a white powder, soluble in ether only after oxidation by the air to ferric pinate.—*Ferric pinate*, obtained by precipitating ferric chloride with pinate of potash, is a brown powder, not sticky at 100°. It contains 4·1 p. c. of ferric oxide, and dissolves in ether with pale-brown, and in oil of turpentine with yellowish-brown colour (Unverdorben).

Pinate of Copper.—Green powder, caking together at 100°, melting to a transparent dark-green resin at higher temperatures, and then decomposing, with formation of cuprous oxide. Contains 7·4 parts of oxide of copper to 100 of pinic acid.—It is insoluble in water, slightly soluble in alcohol and rock-oil, and very easily soluble in ether, oil of turpentine, and fat oils, forming dark-green solutions (Unverdorben).

Pinate of Silver.—Pinate of potash throws down from nitrate of silver, a yellowish powder containing 21 parts of silver oxide to 100 parts of the acid.—The salt is insoluble in water and alcohol, but easily soluble in ether and oil of turpentine.—Caustic potash throws down from the salt, oxide of silver, which re-dissolves on boiling, forming a dark-brown solution, which is not precipitated by chloride of sodium, and therefore probably contains suboxide of silver. The solution yields with acetic acid a brown precipitate, probably of argentous pinate, insoluble in alcohol and ether, but soluble in oil of turpentine and dilute caustic potash; the latter solution may be evaporated down to a brown extract without undergoing decomposition.—The solution of pinate of silver in oil of turpentine turns dark-brown when heated, and deposits on boiling a dark-blue compound of resin with suboxide of silver, which compound is also formed when pinic acid is melted with carbonate of silver (Unverdorben).

Colophony dissolves in *bisulphide of carbon* (Lampadius) in *terchloride of arsenic*, forming a bluish-green solution, which turns brown when heated (Davy).—Pinic acid may be melted together with *oleic* and *stearic acids;* the mixture is not separated by alcohol of 60 p. c. (Unverdorben).—Colophony dissolves in cold *carbolic acid* (Raurge).

On prolonged digestion at a temperature of 15° to 20°, colophony dissolves in 52·5 parts of *alcohol* of 45 p. c., in 26·8 parts of 55 p. c., in 8·3 parts of 71 p. c., and in stronger alcohol so freely that the solution forms a jelly. When excess of colophony is added to alcohol of 71 p. c. the emulsion formed by shaking separates on standing into two layers, the upper of which contains a little colophony with a large quantity of alcohol, whilst the lower consists of clear and liquid colophony with a very small quantity of alcohol. In alcohol of 88 p. c. the excess of colophony does not become liquid (Fluckiger, *Pharm. Viertelj.* 11, 61). — Colophony dissolves easily in *ether*, *wood-spirit*, and *fatty* and *volatile oils*. — When melted together with aloeretic acid it forms a deep-blue mass, having strong colouring properties (Barreswil).

2. Turpentine and Pine-resin.

The resinous juice exuding from incisions in the bark of various species of pine is either rich in oil of turpentine, sticky, and of the consistence of honey (*turpentine*), or it is (as in the case of that obtained from *Pinus Picea*) less oily, and rapidly hardens to a resin. The turpentine exuding from other species of pine, when exposed to the air for some time on the trunk, likewise hardens to *white resin*, *white pitch*, or *galipot*. This last, when subjected to prolonged fusion, whereby oil is volatilised, and pressed through hempen bags, forms *yellow pitch*, whilst by a less prolonged fusion, straining, and subsequent trituration with water till it cools, it is converted into *Burgundy pitch*. — On distilling the turpentines with water, *Terebenthina cocta* remains as a yellow mass of conchoidal fracture, which, when melted alone, loses water and oil, and is converted into colophony.

Turpentine is yellowish-white, transparent, or opaque, of the consistence of honey, sticky, elastic, and is rendered fluid by a gentle heat. It smells and tastes like oil of turpentine, and reddens litmus more strongly than its aqueous decoction. — It is a mixture of oil of turpentine (xiv, 239), and, according to Maly, abietic anhydride (p. 8); according to Unverdorben pinic acid, sylvic acid, and small quantities of other resins; it contains also a little succinic acid, and a small quantity of bitter substance soluble in water. — When distilled alone, turpentine yields, besides volatile oil, a little aqueous acetic acid and needles of succinic acid (Pessina). — It dissolves rapidly in *oil of vitriol;* water throws down from the solution at first a yellow, then a black resin, and lastly a carbonaceous mass, from which alcohol extracts Hatschett's artificial tannin, a brown substance soluble in water and alcohol, and giving a precipitate with gelatin (*N. Gehl.* 1, 155). — Turpentine dissolves slightly in strong, and easily in weak *ammonia*, with the exception of a brown jelly. — It dissolves completely in *caustic potash* not in excess, but the addition of more potash partly precipitates it in white flocks of a potash-compound. The solution may be evaporated at a gentle heat, without loss of oil, to a clear yellow mass, which dissolves easily in water (Berzelius, *Pogg.* 10, 252).

Most of the turpentines rotate a ray of polarised light to the left, a few, however, to the right; the latter yield an oil which exerts less rotatory action than turpentine itself (Biot, *N. Ann. Chim. Phys.*, 10, 11).

a. *Common Turpentine.* — From *Pinus sylvestris.* Opaque, greyish-yellow. Exerts a left-handed action on polarised light (Biot). Contains pinic acid, volatile oil, a little sylvic acid, a trace of a resin insoluble in rock-oil, and a small quantity of extractive matter (Unverdorben).

The *resin from the stem of Pinus sylvestris* is sometimes white and opaque, and consists almost entirely of sylvic acid with a little volatile oil, 8 p. c. of pinic acid, and a trace of extractive; at other times it is translucent and yellow, and then contains 90 p. c. of pinic acid, 9 p. c. of sylvic acid, and a resin insoluble in oil of turpentine, varying in amount from 1 to 25 p. c. (Unverdorben). Transparent drops of pine-resin, dissolved in ether to separate fragments of wood, and recovered from the filtrate on evaporation as a yellow translucent pasty mass, contained 77·46 p. c. C., 9·70 H., and 12·84 O. (Schrötter, *Pogg.* 59, 69).

Pine Mastic.—Occurs in peculiar lumps on the trunks of pine trees, and is distinguishable by the practised eye from ordinary pine-resin. When freed from bark and kneaded into cakes under warm water, it is made use of in Sweden for chewing.—Externally, it is pale, reddish-brown, internally pale, yellowish-brown; it is brittle, and exhibits a milk-white fracture. It tastes balsamic and sour; when chewed it turns soft at first, but afterwards becomes brittle, and of a rose-red colour. When boiled with water, it yields a small quantity of a thick brownish-yellow oil, differing from turpentine; the water takes up a peculiar acid, which is not entirely extracted, even by 16 times repeated boiling. After boiling with water, the resin is completely soluble in alcohol, from which it is precipitated by water as a white or rose-red powder; after fusion it is brittle and no longer softens when chewed, and is susceptible of further decomposition by potash or ammonia (Berlin).

The peculiar acid of pine mastic is deposited from the aqueous decoction, on standing for a week, in rose-red granules; it cannot be obtained pure by evaporating the decoction, and even the crystallised acid is converted into a resin on evaporating its aqueous solution in the air.—The acid reddens litmus, and has a very sour taste. When heated in a glass tube, it melts to a nearly colourless liquid, which solidifies to a crystalline mass, and when more strongly heated gives off empyreumatic oil, leaving charcoal.—The acid dissolves with difficulty in cold, and more easily in hot water. It expels carbonic acid from alkaline carbonates in the cold, forming neutral salts, which give white precipitates with hydrochloric acid. The potash-salt is crystalline. Neutral acetate of lead throws down from strong aqueous solutions of the acid, a salt which dissolves in a larger quantity of water; the basic acetate produces a sulphur-yellow precipitate, even in dilute solutions. The acid precipitates ferric chloride completely, and throws down from acetate of copper a dirty-green, and from nitrate of silver a white precipitate. It dissolves easily in alcohol, and is obtained in radiated crystals on evaporation (Berlin, *J. pr. Chem.*31, 214).

Resins and Wax from the bark of Pinus sylvestris.—*α. Resins.* Obtained by exhausting the powdered bark with ether, shaking the ethereal solution with water to remove brown colouring matter, evaporating the ether, and exhausting the residue with warm alcohol, which takes up resin, leaving wax undissolved. The alcoholic solution is evaporated, and the residue, freed from tannic acid by boiling with water, is dissolved in boiling alcohol. On cooling, the solution deposits white flocks (*a*), melting at 63° to a pale-yellow oil, which solidifies to a yellow translucent brittle resin. — The alcoholic mother-liquor leaves on evaporation a brown, pitch-like sticky mass (*b*), melting at 44·5° (Stähelin & Hofstetter, *Ann. Pharm.* 51, 64).

a contains 74·66 p. c. C., 11·17 H., and 14·17 O.
b „ 73·52 p. c. C., 9·70 H., and 16·78 O.

β. Wax from the bark of Pinus sylvestris. Yellowish, melting at 54°. Smells and tastes aromatic. Evolves an odour of acrolein when heated. Inflammable; not saponifiable; insoluble in ammonia and alcohol, soluble in ether. Contains, on the average, 74·49 p. c. C., 10·30 H., and 15·21 O., corresponding to the formula $C^{96}H^{82}O^{15}$ (or $C^{26}H^{22}O^4$) (Stähelin & Hofstetter, *Ann. Pharm.* 51, 64).

The needles and bark of *Pinus sylvestris* yield also Kawalier's *ceropic acid.* The ceropate of lead obtained in the preparation of kinovous acid (xv, 33) is decomposed under alcohol by hydrosulphuric acid, and filtered boiling; the filtrate deposits the acid on cooling. Ceropic acid is also deposited from an alcoholic decoction of the bark on cooling; and may be obtained from an ethereal extract of the bark by recrystallisation from boiling alcohol (see xv, 34).

Ceropic acid forms microscopic white friable crystals, which melt at 100°, and solidify like bees'-wax on cooling.

		Dried in a vacuum.	Kawalier.	
			a.	*b.*
72 C	432	74·48	74·24	75 55
68 H	68	11·72	12·17	11·32
10 O	80	13·80	13·59	13·13
$C^{72}H^{68}O^{10}$	580	100 00	100·00	100·00

a was obtained from the needles; *b* from the bark.

Ceropate of baryta is precipitated from the alcoholic acid by acetate of baryta (Kawalier, *Wien. Acad. Ber.* 11, 344).

		Dried in a vacuum.	Kawalier.
72 C	432	65·80	65·50
68 H	68	10·36	10 33
10 O	80	12·19	12·65
BaO	76·5	11·65	11·52
$C^{72}H^{68}O^{10}$,BaO	656·5	100·00	100·00

Wax from the exfoliating bark of Pinus sylvestris.—Obtained in the preparation of cortepinitannic acid, and purified by precipitating a hot alcoholic solution with alcoholic neutral acetate of lead, filtering from the grey flocks thrown down, and passing hydrosulphuric acid into the filtrate, from which, after repeated filtration, the wax crystallises. — Melts and solidifies like bees'-wax.

			Kawalier.
32 C	192	75·00	75·07
32 H	32	12·50	12·60
4 O	32	12 50	12·33
$C^{32}H^{32}O^4$	256	100 00	100·00

b. The hardened *white resin* from the trunk of *Pinus picea* (Duroy) contains about 40 p. c. of pinic acid, and 20 p. c. of sylvic acid, together with the following resins and a little volatile oil (Unverdorben, *Pogg.* 11, 41). Fir-resin, in white friable pieces, contains 76·68 p. c. C., 9·42 H., and 13·90 O. (Schrötter).

When an ethereal solution of the hardened resin from the stem is digested with acetate of copper, alpha- and beta-resins are precipitated, whilst gamma- and delta-resins remain in solution. The solution is filtered; the yellowish-green precipitate is decomposed with acids; and the resin thereby separated is boiled with rock-oil, which takes up beta-resin, leaving alpha-resin undissolved.—On evaporating the green ethereal solution, exhausting the residue with 65 p. c. alcohol, which leaves pinate and sylvate of copper undissolved, and evaporating the alcoholic solution repeatedly, to drive off volatile oil, there remains a colourless mixture of gamma- and delta-resin, the former of which is taken up by cold aqueous ammonia.

Alpha-resin resembles colophony, dissolves in aqueous ammonia and potash, and in carbonate of soda when boiled therewith. Very strong potash-ley (containing 50 p. c. of potash) throws down from the alkaline solution a semi-fluid precipitate. The potash-compound is insoluble in alcohol and ether, and precipitates chloride of barium from strong solutions only. The resin dissolves easily in alcohol and ether: its alcoholic solution precipitates neutral acetate of lead brownish, and alcoholic acetate of copper yellowish-green, the latter precipitate being insoluble in ether.—*Beta-resin* is soluble in aqueous ammonia and potash, precipitates alcoholic acetate of copper yellowish-brown, and dissolves in 1,000 parts of rock-oil, from which it is almost entirely deposited in flocks on cooling.—*Gamma-resin* does not precipitate alcoholic acetate of copper. It is soluble in potash-ley and ammonia, and easily soluble in alcohol and ether, but very slightly in rock-oil and oil of turpentine.—*Delta-resin* is insoluble in ammonia (Unverdorben).

c. *Bordeaux Turpentine.*—From *Pinus maritima.* Turbid when fresh, but separates on standing into two layers, the upper of which is transparent and pale yellow, and contains, according to Thénard, 20 p. c. of oil of turpentine, whilst the lower is granular, thick, and opaque.—With half its weight of hydrate of soda it yields a soap which is soft at first and afterwards liquefies. The resin hardens quickly with $\frac{1}{25}$th of magnesia. It dissolves completely in alcohol of 36°, but not perfectly in weaker spirit (Moringlane, Duponchel and Bonastre, *J. Pharm.* 8, 329; Mialhe, *J. Pharm.* 22, 592; Guibourt, *J. Pharm.* 25, 477). It rotates a ray of polarised light to the left, more powerfully than d, but yields an oil which exerts a dextro-rotatory action (Guibourt and Bouchardat). Contains Laurent's pimaric acid (xvii, 323).—The galipot prepared from this resin is completely soluble in alcohol (Guibourt).

d. *Strasburg Turpentine.*—From *Pinus Abies,* Duroy (*Abies pectinata*). Thinner than a; transparent, reddish-yellow or pale-yellow. Levorotatory, less strongly than c (Guibourt & Bouchardat, *N. J. Pharm.* 8, 18). Does not harden with magnesia (Soubeiran).

The colourless, transparent, very fluid turpentine of the Vosges (from *Abies pectinata*) contains 23·5 p. c. of volatile oil, 63·44 p. c. of resin, 0·85 extractive and succinic acid (Caillot). Sell and Blanchet obtained nearly the same quantity of volatile oil. The water remaining upon the colophony from which the turpentine has been distilled has not an acid reaction; it produces a precipitate with basic acetate of lead and iron-salts, with ammonia only after evaporation, probably owing to the presence of a resin-acid. — By distillation and repeated boiling of the residue with water, the turpentine yields a yellow transparent colophony, containing 78·16 p. c. C., 10·08 H., and 11·76 O. (Sell and Blanchet, *Ann. Pharm.* 6, 269.)

That portion of the resin of *Pinus Abies* which is soluble in cold alcohol remains, on evaporating the solution, as a pale yellow brittle mass, melting at 100°, and containing 74·56 to 75·16 p. c. C., and 9·25 to 9·35 H., corresponding to the formula $C^{40}H^{29}O^6$. — The portion sparingly soluble in cold alcohol, when purified by solution in hot alcohol and partial evaporation, melts at 149°, and contains, on an average, 76·98 p. c. C., and 9·40 H., corresponding to the formula $C^{40}H^{29}O^5$ (Johnston, *Phil. Trans.* 1839, 298).

Strasburg turpentine from *Abies pectinata*, Vosges turpentine from *Abis excelsa*, and that of *Balsamea canadensis* contain a neutral resin, abietic acid, and abietin. — To separate these bodies, the turpentine is distilled with water, and the residue is treated with cold alcohol, which leaves the *resin* undissolved in the form of a white non-crystalline powder, tasteless, neutral, insoluble in alkalis, in cold alcohol of 40°, and in rock-oil. — The residue which is left on evaporating the alcoholic solution, when mixed with twice its weight of carbonate of potash and boiled with water, deposits a mixture of abietin and abietic acid, which is to be agitated with 30 parts of water; the abietin then remains undissolved, and the abietic acid may be precipitated from the filtrate by acids.

Abietin forms rectangular needles arranged in tufts, melting even on exposure to sunshine to a colourless oil, which crystallises on cooling. It is neutral to litmus. — It is insoluble in water, and is not altered by standing for half a year in potash-ley. It dissolves very easily in strong acetic acid, alcohol of 44°, ether, and rock oil, crystallising on evaporation.

Abietinic acid cakes together at 55° in a colophony-like mass. Tastes slightly bitter, and reddens litmus when warm. In combining with bases it loses about 5 p. c. of water. The ammonia-salt does not crystallise, and loses its ammonia immediately when heated. The acid melts with $\frac{1}{2}$ part of hydrate of potash to a friable mass, which remains in the form of a jelly on evaporating its alcoholic solution. The insoluble baryta-salt contains 40 p. c. of baryta. The acid dissolves in all proportions of alcohol, ether, and rock-oil. It forms with quinine and morphine, white salts insoluble in water, but soluble in alcohol and ether, from which they do not crystallise (Caillot, *J. Pharm.* 16, 436).

c. *Venice Turpentine.* — From *Pinus Larix*. Pale-yellow, transparent, less tenacious and of more agreeable odour than common turpentine. It contains oil of turpentine, a large quantity of pinic acid, a neutral resin, traces of a second resin insoluble in rock-oil, succinic acid, and a little extractive bitter, which precipitates neutral acetate of lead, turns brown in the air, and is insoluble in water (Unverdorben). It does not harden with $\frac{1}{16}$th of magnesia (Guibourt, Soubeiran). Forms a hard soap with hydrate of soda. — It dissolves completely in alcohol (Guibourt), but after being kept under water for a year, at

60° to 100°, it is insoluble in alcohol and resembles amber (Göppert, *J. pr. Chem.* 42, 57).

The *neutral resin of Venice turpentine* remains in solution after precipitating the pinic acid with alcoholic acetate of copper (p. 9). The filtrate is evaporated, and the residue, freed from excess of acetate of copper by means of water, is dissolved in a small quantity of alcohol, filtered, and boiled with water, whereby the resin is thrown down in a semi-fluid mass, which is freed from adhering pinic acid by washing with potash-ley. — The resin is colourless and hard, but softens to a tenacious mass in the mouth. It does not combine with potash or other bases, but dissolves in a strong aqueous solution of pinate of potash, from which it is partially precipitated by water. — It dissolves in all proportions of alcohol, ether, rock-oil, and other oils (Unverdorben).

f. *Canada Turpentine.* — From *Pinus* or *Abies balsamea.* Pale-yellow, highly-transparent, thin, but very tenacious. Smells and tastes more agreeable than the other varieties of turpentine. Rotates a ray of polarised light to the right (Guibourt & Bouchardat). Contains $\frac{3}{4}$ths to $\frac{3}{8}$ths of a resin sparingly soluble in alcohol (Bonastre, *J. Pharm.* 8, 574). Yields with soda a soft soap, which does not liquefy. — The same tree yields the *spurious Mecca balsam*, which exudes from incisions made into enlargements under the bark.

g. *Carolina turpentine.* — From *Pinus taeda.* Commercial English turpentine. Very thick at 10°, opaque, and of a pale, amber-yellow colour. After filtration while warm, it deflects a ray of polarised light to the left, as does also the volatile oil obtained from it (Guibourt & Bouchardat).

h. *Resin of Araucaria Brasiliana* (Conifers). — Exudes from old trees, especially after the bark has been damaged by beetles, and hardens rapidly in the air. Dull-white or dark-brown irregular pieces, varying in size from that of a bean to that of a walnut, and elongated drops. Has a faint lustre and a smooth waxy fracture. Smells balsamic, somewhat turpentine-like, and tastes resinous, biting, and aromatic. Sticks to the teeth. — Heated on platinum foil it carbonises without melting completely, evolving an odour of incense. In a flame it takes fire and burns, leaving 5 p. c. of ash. — The resin dissolves to the extent of about $\frac{2}{3}$rds in water, and $\frac{1}{3}$rd in alcohol; ether and chloroform take up only traces of volatile oil. — It contains volatile oil, gum, and vegetable albumin, uncrystallisable sugar, and four different resins. — From the mixture of resins, freed from volatile oil and substances soluble in water, cold alcohol takes up alpha-, beta-, and gamma-resin, leaving araucaric acid undissolved. The gamma-resin is precipitated from the alcoholic solution by acetate of copper, and the beta-resin from the filtrate by alcoholic neutral acetate of lead, whilst the alpha-resin remains in solution.

Alpha-resin or Curic acid. — Pale-brown resin of the consistence of turpentine, and having a faint odour of that substance. Melts on platinum-foil, and burns with smoky flame, emitting an odour of incense. It is insoluble in aqueous carbonate of soda, and only very slightly soluble in ammonia and potash- or soda-ley. The alcoholic solution is not precipitated by ammonio-nitrate of silver; on boiling it therewith silver is thrown down. It does not precipitate cupric or plumbic salts, but gives a yellow precipitate with ferric salts. It dissolves in ether, chloroform, and absolute and ordinary alcohol.

Beta-resin or *Curiuvic acid* is separated from the lead-salt by hydrosulphuric acid. Brown, inodorous and tasteless, triturable to a yellow powder, soft, and sticky between the fingers. The alcoholic solution has an acid reaction, and precipitates neutral acetate of lead white, and sesquichloride of iron and nitrate of silver pale-yellow. The resin dissolves in aqueous ammonia, from which it is precipitated by hydrochloric acid, and slightly in potash- and soda-ley. It is sparingly soluble in bisulphide of carbon; easily soluble in ether, chloroform, and alcohol; insoluble in fixed and volatile oils.

Gamma-resin or *Pinonic acid.* — Yellow, friable pieces, easily fusible, inflammable, and burning with a luminous flame. Acid in alcoholic solution. Dissolves in aqueous ammonia, and easily in ether, alcohol, and volatile oils.

Araucaric acid.—This body is extracted by boiling alcohol from the resin previously exhausted by cold alcohol, and is deposited on cooling in the form of a yellow powder, which may be decolorised by again dissolving it in alcohol. —White, indistinctly crystalline granules, easily fusible, and burning with flame. It is insoluble in aqueous ammonia; but on evaporating a mixture of the alcoholic acid and ammonia, it remains as a colourless alkaline ammonia-salt, which is insoluble in water and ether — The acid is insoluble in boiling aqueous carbonate of soda; the soda-salt obtained from an ethereal solution of the acid mixed with soda-ley, is a white amorphous powder, insoluble in water and ether, but easily soluble in alcohol. The white amorphous lime-salt precipitated from an alcoholic solution of the acid by alcoholic chloride of calcium is easily soluble in alcohol (!), insoluble in ether.— The acid dissolves in cold absolute alcohol, and in boiling alcohol of sp. gr. 0·837; it is easily soluble in ether, chloroform, and volatile oils (Peckolt, *N. Br. Arch.* 122, 225).

i. *Resins from Oil of Turpentine.* — The products formed from oil of turpentine by exposure to the air (xiv, 245), or by the action of nitric acid (xiv, 249) bear no perceptible relation to the pine-resins.— When oil of turpentine is allowed to resinise in the air, formic acid is among the products obtained. The colophony-like mass does not yield abietic acid (Maly).

On dropping oil of turpentine in small portions into nitric acid, and heating so long as red fumes are emitted, an acid solution and a mixture of resins are obtained. The latter is either (after short exposure to the action of the acid) red-brown, soft, and almost entirely soluble in alcohol, or (after prolonged boiling) yellow and friable. In the latter case a solution of the resin in boiling alcohol deposits terepthalic acid (xiii, 13), whilst the residue left on evaporation gives up to boiling water terebenzic acid (xvi, 183), three other resins free from nitrogen remaining undissolved.

a. Alpha-resin. — Insoluble in cold, but soluble to a slight extent in boiling alcohol, from which it is deposited as a yellow, amorphous powder. Insoluble in ammonia and caustic potash. Melts above 100°.

When purified by washing with warm alcohol and ammonia, it contains 56·36 p. c. C., 5·65 H., and 37·99 O., corresponding to the formula $C^{40}H^{24}O^{20}$ (calc. 56·60 C., 5·66 H.).

b. *Beta-resin.* — Soluble in cold alcohol, but insoluble in ammonia and caustic potash. Melts below 100°. Contains, after drying at 100°, 70·12 p. c. C., 7·31 H., and 22·57 O., agreeing therefore with the formula $C^{40}H^{24}O^{10}$ (calc. 69·77 C., 6·97 H.).

c. *Gamma-resin.* Semifluid at 100°. Soluble in cold alcohol, and in ammonia and caustic potash. Contains, after drying at 100°, 61·66 p. c. C., 6·21 H., and 32·63 O., corresponding to the formula $C^{40}H^{24}O^{16}$ (calc. 61·22 C., 6·12 H.) (Caillot, *N. Ann. Chim. Phys.* 21, 36).

Oxyazo-nucleus $C^{48}NH^{33}O^4$.

Delphinine.

$$C^{48}NH^{35}O^4 = C^{48}NH^{33}O^4,H^2.$$

BRANDES. *Schw.* 25, 369; *N. Tr.* 3, 2, 165.
LASSAIGNE AND FENEULLE. *Ann. Chim. Phys.* 12, 358; *Gilb.* 62, 375; *N. Tr.* 4, 2, 199.
FENEULLE. *J. Pharm.* 9, 4; *Schw.* 42, 116.
O. HENRY. *J. Pharm.* 18, 663; 19, 593; *Repert.* 44, 73; *Schw.* 68, 77; *N. Tr.* 26, 2, 240.
COUERBE. *Ann. Chim. Phys.* 52, 359; *J. Pharm.* 19, 519; *Ann. Pharm.* 6, 100.
J. ERDMANN. *N. Br. Arch.* 117, 43; *N. Repert.* 13, 86.

Delphine. Discovered by Brandes and by Lassaigne and Feneulle simultaneously, in 1819, in the seeds of *Delphinium Staphisagria*, but first distinguished and separated from staphisagrine by Couerbe. Occurs in the seeds to the amount of $\frac{1}{10}$th p. c. (Erdmann); more abundantly in the grey or brown than in the black seeds (Couerbe).

Preparation. 1. Powdered stavesacre seeds, made into a pulp with a moderate quantity of water, are heated in a water-bath for some days and pressed while still warm to remove the greater part of the fat, by which process but little delphinine is lost, if the quantity of water employed be not too great. The residual mass, digested with strong alcohol for six or eight hours and pressed, yields a tincture from which the alcohol is distilled. There then remains an oily resinous mass from which the alkaloids are separated by treating it with weak hydrochloric acid, precipitating the filtrate with ammonia, washing, and drying. The mixture of bases thus obtained is treated with ether, when impure staphisagrine is left in the form of a brown resin, whilst the delphinine is dissolved. The latter body is recovered by evaporating the solution, dissolving the residue in hydrochloric acid, precipitating with ammonia, washing, drying, again dissolving in ether, and evaporating (J. Erdmann).

2. An extract of the seeds, prepared with boiling alcohol, is boiled with water containing sulphuric acid; the solution, separated from

fat, is precipitated with caustic potash or ammonia; and the precipitate is dissolved in boiling alcohol, decolorised by animal charcoal, and evaporated. The residue is a mixture of delphinine, staphisagrine, and resin, which is dissolved in dilute sulphuric acid, and freed from resin by dropping into it moderately strong nitric acid. After standing 24 hours, the liquid is decanted and precipitated with caustic potash; the precipitate is dissolved in alcohol; the solution is evaporated; and the residue is treated first with boiling water, to remove a little saltpetre, and then with ether to separate the delphinine and staphisagrine (Couerbe).

Kukla (*Zeitschr. Phys. v. W.* 5, 339) boils bruised stavesacre seeds with very weak sulphuric acid; precipitates the decoction with ammonia; dries the precipitate and exhausts it with alcohol; distils off the alcohol; evaporates the residue to the consistence of honey; and shakes it with ether. On evaporating the ether, the delphinine remains as a white resin. — In the processes of Brandes, Lassaigne and Feneulle, and Henry, the separation of staphisagrine is not provided for.

Properties. Delphinine forms an amorphous white mass, of persistent bitter taste, strongly alkaline in solution (Erdmann, Couerbe). According to Couerbe, it melts at 120° — Concerning the detection of delphinine under the microscope, see Erhard (*N. Jahrb. Pharm.* 25, 286).

	at 100°.		Couerbe.	Henry.	Erdmann.
48 C	288	78·04	75 60	76·55	77·62
N	14	3·79	5·84	5 58	3·74
35 H	35	9·49	8 89	8 81	9 38
4 O	32	8 68	9 67	9·06	9·26
$C^{48}NH^{35}O^{4}$	369	100·00	100 00	100·00	100·00

According to Henry and Couerbe, the formula is $C^{27}NH^{19}O^{2}$; Erdmann's analysis led to the above formula.

Decompositions. Delphinine undergoes decomposition at a temperature above its melting point, leaving a large quantity of charcoal. — It is coloured red, and afterwards carbonised by *oil of vitriol* (Couerbe); according to Henry it is coloured at first red and after 24 hours brown. — It is coloured green by oil of vitriol and bichromate of potash (Eboli). — Hot *nitric acid* converts delphinine into a resin (Couerbe). Nitric acid colours aqueous hydrochlorate of delphinine yellow, on boiling only, whereupon stannous chloride throws down yellowish-white flocks (v. Planta). — *Chlorine* does not act on delphinine at ordinary temperatures, but attacks it violently at 150° to 160°, forming hydrochloric acid, and a green, afterwards dark-brown, friable mass, which is only partially soluble in alcohol and ether (Couerbe).

Combinations. Delphinine is nearly insoluble in *water*, but the water acquires a very bitter taste (Lassaigne and Feneulle), and after boiling with it becomes turbid on cooling (Brandes).

Tincture of iodine throws down from hydrochlorate of delphinine a brown precipitate (v. Planta).

Delphinine forms with *acids* amorphous deliquescent salts. Ammonia, potash, carbonate of ammonia, the carbonates and bicarbonates of the alkalis [not the latter (Kletzinsky)] precipitate delphinine from the hydrochlorate in the form of a flocculent or gelatinous precipitate, insoluble in excess of the precipitant. Phosphate of soda gives with the hydrochlorate a precipitate which is pulverulent in strong and gelatinous in weak solutions (v. Planta).

When exposed to a current of *hydrochloric acid gas* 100 parts of delphinine take up 17·52 parts of the acid (Couerbe).

Hydrochlorate of delphinine gives with *iodide of potassium* a yellowish-white precipitate (v. Planta); with *phosphomolybdic acid* a greyish-yellow (Sonnenschein), with *idomercurate of potassium* a yellowish precipitate, insoluble in hydrochloric acid; with *mercuric chloride* a white pulverulent precipitate (v. Planta).

Chloroplatinate of Delphinine. — Chloride of platinum throws down from hydrochlorate of delphinine a dense yellow powder, easily soluble in hydrochloric acid (v. Planta). Faint yellow precipitate, nearly white when dry, insoluble in water, alcohol, and ether (Erdmann).

	at 100°.		Erdmann.
48 C	288	50·05	49·62
N	14	2·43	2·94
36 H	36	6·25	6·47
4 O	32	5·56	5·08
3 Cl	106·5	18·50	18·73
Pt	99	17·21	17·16
$C^{48}NH^{35}O^4,HCl,PtCl^2$	575·5	100·00	100·00

Chloride of iridium and sodium throws down from hydrochlorate of delphinine reddish-brown flocks, insoluble in hydrochloric acid. *Chloride of gold* produces a sulphur-yellow, *sulphocyanate of potassium* a bright red, and *picric acid* a dense yellow precipitate. *Tincture* and *infusion of galls* produce a turbidity in hydrochlorate of delphinine, after which a little hydrochloric acid throws down a dense precipitate (v. Planta).

Delphinine dissolves in *ether* and more freely in *alcohol* (Couerbe). It is sparingly soluble in creosote (Reichenbach).

Staphisagrine.

COUERBE. *Ann. Chim. Phys.* 52, 363.

Staphisaïne. — Obtained from stavesacre seeds simultaneously with delphinine and remains undissolved on treating the mixture of the two bases with ether. — Solid yellow mass, of very acrid taste. Melts at 200°, and afterwards decomposes, with evolution of ammonia, leaving a large quantity of charcoal.

	According to Couerbe.		Couerbe.
32 C	192	73·56	72·67
N	14	5·36	5·78
23 H	23	8·81	8·72
4 O	32	12·27	12·83
$C^{32}NH^{23}O^4$	261	100·00	100·00

Staphisagrine is converted into a resin by *nitric acid*, and is decomposed by *chlorine* only when heated. It is nearly insoluble in *water*, but dissolves in aqueous *acids*, without forming definite salts. Soluble in *alcohol*, insoluble in *ether*.

Primary Nucleus $C^{48}H^{40}$; *Oxygen-nucleus* $C^{48}H^{38}O^{2}$.

Kinovic Acid.

$$C^{48}H^{38}O^{8} = C^{48}H^{38}O^{2},H^{6}.$$

HLASIWETZ. *Ann. Pharm.* 111, 182.
DE VRIJ. *N. J. Pharm.* 37, 255.

Occurs together with kinovin in the East Indian cinchona trees (D. Vrij); also in the root of *Potentilla Tormentilla* (Rembold, *Ann. Pharm.* 145, 5). — It is formed together with kinova-sugar (xv, 345) on boiling kinovin with alcoholic hydrochloric acid:

$$C^{60}H^{48}O^{16} + 2HO = C^{48}H^{38}O^{8} + C^{12}H^{12}O^{10} \text{ (Hlasiwetz).}$$

Preparation. 1. Dry hydrochloric acid gas is passed into a solution of kinovin in strong alcohol, whereupon the liquid becomes hot and deposits a white crystalline powder, which is purified by washing it with weak spirit and recrystallising from a large quantity of boiling alcohol. The mother-liquors yield a further quantity after distilling off the alcohol (Hlasiwetz).

¶ According to Rochleder (*Wien. Acad. Ber.* 56, 2 *Abth.* 97; *Jahresb.* 1867, 749) kinovic acid is produced by treating kinovin with sodium amalgam and alcohol. The kinovin then dissolves (with the exception of a few flocks of a brownish waxy substance), forming a brownish liquid, which on evaporation leaves crystalline kinovate of soda. The pure salt separated from the mother-liquor, and decomposed in alcoholic solution with hydrochloric acid, yields pure kinovic acid.

2. Tormentil root is twice exhausted by boiling with thin milk of lime, the filtrate is acidulated, the washed precipitate boiled with baryta-water, the filtered solution again precipitated with hydrochloric acid, the washed precipitate dissolved in a large quantity of hot alcohol, and the reddish solution decolorized with animal charcoal. On distilling off part of the alcohol, pure kinovic acid separates as a colourless sandy crystalline powder (Rembold).¶

Properties. Dazzling-white loose crystalline powder, consisting, according to Grailich, of microscopic six-sided laminæ of the right prismatic system. Tasteless (Hlasiwetz). In ammoniacal solution it exerts a right-handed action on polarised light, $[\alpha]\,j = 76{\cdot}5°$ (De Vrij). It does not lose weight at 140° after drying at 100° (Hlasiwetz).

	Dried at 100°.		Hlasiwetz. *mean.*
48 C	288	73·84	73·60
38 H	38	9·74	9·85
8 O	64	16·42	16·55
$C^{48}H^{38}O^{8}$	390	100·00	100·00

Decompositions. 1. Kinovic acid melts when heated, afterwards solidifying to a fissured mass; when more strongly heated it evolves vapours smelling like incense, and burns with flame. — 2. Submitted to *dry distillation* it yields a thin oil, smelling of turpentine, then an odour of incense, and an amber-yellow thick resinous distillate. — 3. In contact with *pentachloride of phosphorus*, it becomes fluid, evolves hydrochloric acid, and at the temperature of 110° yields a distillate of chlorophosphoric acid, the residue turning thick and violet. The violet mass is decomposed by alcohol, and on addition of water throws down coloured kinovic acid; it froths up when heated, evolving acid vapours, and leaves charcoal. — 4. Kinovic acid is scarcely affected by *hydrochloric acid*, or by boiling *nitric acid* (Hlasiwetz).

Combinations. Kinovic acid is quite insoluble in *water*. — It dissolves in *oil of vitriol*, and is precipitated from the solution unaltered by water (Hlasiwetz). The solution, the formation of which is attended by a slight evolution of gas, is at first brown, afterwards red (De Vrij). — Kinovic acid forms with *bases*, bi-acid salts having the general formula $C^{48}H^{35}M^2O^8$. It dissolves in aqueous ammonia, and in caustic alkalis and their carbonates, expelling carbonic acid from the latter (Hlasiwetz).

Ammonia-salt. — The solution loses ammonia when evaporated, and dries up to a varnish.

Potash-salt. — Strong potash-ley throws down from a strong aqueous solution of the ammonia-salt a pasty mass, which is to be pressed till it appears dry and friable — The salt is also deposited in the form of a jelly on boiling a solution of the acid in dilute caustic potash. — It gives off its water with difficulty, at about 160° only, and is coloured by a stronger heat (Hlasiwetz).

	at 160°.		Hlasiwetz.
48 C	288	58·37	58·11
39 H	39	7·91	7·80
9 O	72	14·59	14·99
2 KO	94·4	19 13	19 10
$C^{48}H^{36}K^2O^8$ + 3 aq.	493·4	100·00	100 00

Baryta- strontia-, and *lime-salts* are obtained by double decomposition, and are deposited from dilute solutions after standing for some time, and from strong or hot solutions in the form of jellies.

Copper-salt. — Obtained by precipitating the ammonia salt with sulphate of copper. Bright-blue precipitate containing, after drying at 120°, 34·71 p. c. C., and 37·38 CuO, agreeing approximately with the formula $C^{48}H^{36}Cu^2O^8 + 6(CuO,HO) + 10$ aq. (calc. 34·54 p. c C., 38·09 CuO).

Silver-salt. — The ammonia-salt throws down from nitrate of silver a copious precipitate, which must be washed in the dark and dried first in a vacuum, afterwards at 120°. In the moist state it blackens very rapidly on exposure to light.

	at 120°.		Hlasiwetz.
48 C	288	47·68	47·56
36 H	36	5·96	6·35
2 Ag	216	35·76	35·33
8 O	64	10 60	10·76
$C^{48}H^{36}Ag^2O^8$	604	100·00	100·00

Kinovic acid dissolves very slightly in cold, and rather more freely in boiling *alcohol*. It is very sparingly soluble in *ether* (Hlasiwetz), and insoluble in *chloroform* (De Vrij).

Glucoside of Kinovic Acid.

Kinovin.

$$C^{60}H^{48}O^{16} = C^{12}H^{12}O^{10},C^{48}H^{36}O^{6}.$$

PELLETIER AND CAVENTOU (1821). *J. Pharm.* 7, 112; *N. Tr.* 6, 1, 90.
F. L. WINCKLER. *Repert.* 49, 116.—Further 51, 193.—75, 293.—81, 42, 51, and 332.—91, 314.—*Repert.* (3) 4, 206.
L. A. BUCHNER. *Repert.* 53, 1; *Ann. Pharm.* 17, 161.
PETERSEN. *Ann. Pharm.* 17, 164.
SCHNEDERMANN. *Ann. Pharm.* 45, 277; *Repert.* 81, 45; *J. pr. Chem.* 28, 327.
HLASIWETZ. *Wien. Acad. Ber.* 6, 278; *Ann. Pharm.* 79, 145; *J. pr. Chem.* 55, 411; *Chem. Gaz.* 1851, 421 and 441; *Kopp's Jahresber.* 1851, 413.—*Wien. Acad. Ber.* 35, 503; *Ann. Pharm.* 111, 182; *J. pr. Chem.* 78, 104; *N. Ann. Chim. Phys.* 57, 360; *Kopp's Jahresber.* 1859, 578.
R. SCHWARZ. *Wien. Acad. Ber.* 7, 247; *J. pr. Chem.* 56, 76; abstr. *Ann. Pharm.* 80, 330; *Pharm. Centr.* 1852, 193; *Kopp's Jahresber.* 1851, 411.
DE VRIJ. *N. J. Pharm.* 37, 255; *N. Repert.* 9, 303; *N. Jahrb. Pharm.* 14, 251; *Pharm. Viertelj.* 14, 221 and 231; *Pharm. J. Trans.* 5, 593 and 6, 18; *Kopp's Jahresber.* 1859, 578.

Kinovic acid, Kinova bitter, Acide Kinovique.—Discovered by Pelletier and Caventou; investigated chiefly by Hlasiwetz.—Buchner, jun., regarded kinovin as identical with pariglin (xvi. 99), which view was controverted by Petersen, Winckler, and Schnedermann.—Kinovin agrees in many respects with chiococcic acid, and was formerly regarded as identical with that body by Hlasiwetz (*Wien. Acad. Ber.* 6, 278), who now, however, doubts the identity (*Ann. Pharm.* 111, 182).—*Naucleic acid*, discovered by Bernelot-Moens in Batavia, is, according to De Vrij, identical with kinovin.

Source. In the bark of *China nova* (Pelletier and Caventou Winckler). Also in the true cinchona-barks (Winckler), especially in the following: *China Huamalies*, *C. flava dura*, *C. nova flava*, *C. Rio de Janeiro*, *C. alba*, *C. de Maracaibo*, *C. Piton s. St. Luciæ*, and in the closely allied *Cortex Esenbeckiæ febrifugæ*, in the red or dark *Parachina* (Winckler). In *China regia* (Schwarz) and *C. fusca* (Hlasiwetz, Winckler). In the cinchona barks of the *Iles des Lagos* in Upper Guiana (Klöte-Nortier, *N. Br. Arch.* 93, 25).

All parts of the cultivated East Indian cinchona trees contain kinovin and kinovic acid. *Cinchona Calysaya* contains in the wood of the root 2·57 p. c., in the bark of the root 1·08, in the wood of the trunk 1·80, in the bark of the trunk 0·36, in the bark of the branches 0·68, in the twigs 0·85, in the leaves 0·23 p. c. of the two substances.

According to Winckler (*Pharm. Centr.* 1851, 703) *Secale cornutum* contains kinovin.

Preparation. 1. A decoction of kinova bark, obtained by repeatedly boiling the bark with water and one-tenth its weight of hydrate of lime, is mixed with excess of hydrochloric acid; the precipitate thus formed is collected, washed with cold water, and dissolved in warm aqueous ammonia [or in milk of lime (Hlasiwetz)]; the dark solution is digested with animal charcoal, and filtered; the filtrate is again precipitated with hydrochloric acid; the precipitate is washed, dried, triturated, and dissolved in 90 p. c. alcohol, and the solution is decolorized by animal charcoal and evaporated (Winckler). It is better to employ bark which has been previously exhausted with water, and thereby freed from the greater part of the kinova red contained in it (Hlasiwetz) — Kinovin thus obtained contracts into a tough mass when treated with weak spirit, owing to the presence of a foreign substance, to remove which Schnedermann shakes it with warm alcohol of 60° to 65°, and precipitates the filtrate with boiling water, repeating this operation till the product is perfectly pure.

2. An alcoholic extract of kinova bark is precipitated with neutral acetate of lead; the filtrate is freed from excess of lead by hydrosulphuric acid; the greater part of the alcohol is distilled off, and the residue is poured into water, whereupon kinovin is precipitated and may be purified as in 1 (Hlasiwetz).

3. Powdered cinchona-bark is treated with cold very weak soda-ley; the extract is precipitated with hydrochloric acid; the precipitate is dissolved in milk of lime, to separate red colouring matter, and the filtrate is precipitated, while still hot, with hydrochloric acid. The precipitate is purified by repeated solution in milk of lime, and precipitation by hydrochloric acid. It is a mixture of kinovin and kinovic acid, the former of which is dissolved by chloroform (De Vrij).

Pelletier and Caventou dissolve the alcoholic extract of kinova bark in water; agitate the solution with magnesia, and precipitate the filtrate with an acid. A similar process is employed by Winckler, who obtains a further quantity of kinovin from the residue left on treating the alcoholic extract with water, by mixing it with animal charcoal, exhausting with ether, and evaporating. — Winckler exhausts with ether the bark of *Esenbeckia febrifuga* (to which the first method is not applicable), decolorises the ethereal solution with animal charcoal, and evaporates, when kinovin remains. He further treats the residual bark with 96 p. c. alcohol, shakes the tincture with lime, evaporates the filtrate, and agitates the residue with ether, which takes up kinovin. The whole of the kinovin thus obtained requires further purification.

Properties. Kinovin forms an amorphous, nearly transparent resin, triturable to a light, white powder. The earlier statements as to the crystallisation of kinovin, and probably also those of Winckler (*Jahrb. pr. Pharm.* 18, 379), seem to refer to kinovic acid. — Inodorous, or smells faintly balsamic when warmed. Tasteless at first, but afterwards very persistently and disagreeably bitter and acrid. Neutral. Electric when rubbed (Winckler, Hlasiwetz). — In alcoholic solution it exerts a dextro-rotatory action on polarised light; $[\alpha]\ j = 52{\cdot}4$ (De Vrij).

Kinovin may be obtained in the anhydrous state by keeping it in a vacuum for a month, but cannot be dehydrated at once, even at a temperature of 190°: kinovin dried at 100° to 140° contains from 1 to 2 atoms of water, which is given off at 160° to 180° (Hlasiwetz). According to Buchner, kinovin dried in a vacuum loses 8·53 p. c. of water at 120°, and according to Schnedermann no more before undergoing decomposition.

Calculations according to Hlasiwetz.

a.			*b.*		
60 C	360	67·16	60 C	360	68·31
48 H	48	8·95	47 H	47	8·91
16 O	128	23·89	15 O	120	22·78
$C^{60}H^{48}O^{16}$	538	100·00	— HO	527	100·00

c.		
60 C	360	69·49
46 H	46	8·88
14 O	112	21·63
$C^{60}H^{48}O^{16}$–2 HO	518	100·00

	Petersen.	Schnedermann. *dried.*	Schwarz. *at* 100°.	Hlasiwetz. *at* 100°.	*at* 140°.	*at* 180°.
C	66·65	67·13	68·89	66·05	66·57	68·33
H	8 94	8·98	8 86	8 93	8 88	9·03
O	24 41	23·89	22 25	25 02	24·55	22 64
	100 00	100·00	100 00	100·00	100 00	100·00

According to Petersen, the formula is $C^{15}H^{12}O^{4}$; according to Schnedermann $C^{38}H^{30}O^{10}$. — Hlasiwetz's third analysis corresponds with the formula *b*; that of Schwarz with *c*, both of which are derived from *a* by the abstraction of 1 or 2 atoms of water.

Decompositions. 1. Kinovin when *heated*, melts to a pale-yellow thick liquid, which solidifies to a friable resin on cooling. When more strongly heated it boils, evolves a peculiar odour, takes fire, and burns with a red smoky flame (Winckler). Submitted to dry distillation, either alone or mixed with sand, it yields an acid [acetic acid (Buchner)], an empyreumatic thin turbid liquid containing aldehyde, and afterwards an amber-yellow heavy liquid, which solidifies to a resin containing, after solution in alcohol and evaporation, 85·44 p. c. C., 10·93 H., and 3·63 O. — Kinovin mixed with lime and subjected to dry distillation yields water, then yellow metacetone, and lastly the above resin (Hlasiwetz). — 2. *Oil of vitriol* poured upon kinovin colours it brown and gradually dissolves it, with dark-red colour (Winckler). The solution is brown at first, but changes to blood-red, fine red-brown, and ultimately a paler colour. Water throws down from the red solution apparently unchanged kinovin, and from that which has become paler, kinovin which is no longer bitter (Buchner). — Kinovin dissolved in alcohol breaks up into kinovic acid and kinova-sugar (xv, 345) on passing *hydrochloric acid gas* into the solution;

$$C^{60}H^{48}O^{16} + 2HO = C^{18}H^{38}O^{8} + C^{12}H^{12}O^{10} \text{ (Hlasiwetz).}$$

4. Kinovin dissolves in boiling *nitric acid* with yellow colour, leaving a white granular powder. When the solution is heated til the red fumes disappear, water throws down white flocks, which, when dissolved in hot alcohol and evaporated, yield a pale-yellow resin (containing 60·94 p. c. C., 6·67 H., and 32·39 O.), and a powder insoluble in alcohol (containing 58·25 p. c. C., 6·10 H., and 35·55 O.) (Hlasiwetz). For the former body Hlasiwetz gives the formula $C^{20}H^{13}O^{6}$ and for the latter $C^{24}H^{15}O^{11}$. Kinovin dissolves in strong nitric acid, forming a brown solution, from which it is precipitated unaltered by water, and which contains no oxalic acid (Buchner).

Combinations. Kinovin is nearly insoluble in cold, and but little soluble in boiling *water* (Buchner). The solution froths strongly when shaken (Buchner). It is insoluble in dilute acids (Winckler); not more soluble in dilute *hydrochloric acid* than in water (Schnedermann)

Kinovin combines with *bases* (Winckler and others). Its combinations with ammonia, the alkalis, and magnesia [formerly, up to the investigation of Hlasiwetz (*Ann. Pharm.* 111, 182) described as salts of kinovic acid] taste very bitter, dissolve very easily in water and alcohol, have a faint alkaline reaction, and are decomposed by acids, including carbonic acid, with separation of kinovin (Schnedermann).

The solution of kinovin in aqueous *ammonia* leaves kinovin free from ammonia on evaporation. The easily formed solution in *potash-ley* leaves a pale-yellow amorphous mass (Schnedermann). — The *baryta-compound* is soluble in alcohol and ether (Pelletier & Caventou).

Kinovin and Lime. — Occurs in kinova bark (Hlasiwetz). — Lime-water or milk of lime dissolves kinovin easily (Winckler); on evaporating the solution, there remains a flocculent mass, the strong aqueous solution of which turns pasty when heated, and recovers its clearness and mobility on cooling (Schnedermann).

Kinovin and Magnesia. — Obtained by boiling kinovin with magnesia and water. On evaporating the solution, it collects on the surface of the liquid in the form of a colourless pellicle, having a fatty lustre, and is ultimately left in light white spangles. — Very bitter (Schnedermann). Dissolves easily in alcohol and ether (Pelletier & Caventou).

Kinovin and Lead-oxide. — An alcoholic solution of kinovin evaporated repeatedly over oxide of lead, leaves a residue, which is for the most part taken up again by alcohol (Schnedermann). Alcoholic kinovin throws down from an alcoholic solution of neutral acetate of lead, a white precipitate which partially disappears on agitation. After a time another precipitate appears in abundance, the liquid becoming pasty, or with stronger solutions solidifying to a jelly. The first precipitate appears to be a compound of kinovin and lead-oxide, the second (some of which is always mixed with the first, even when the liquid is filtered rapidly) contains also acetate of lead (Schnedermann).

	With two atoms of lead oxide.		Schnedermann. *mean.*
60 C	360	47·37	46·38
48 H	48	6·31	6·04
16 O	128	16·84	16 83
2 PbO	224	29·48	30 75
$C^{60}H^{48}O^{16},2PbO$	760	100·00	100 00

According to Schnedermann, $2(C^{38}H^{29}O^{9},PbO) + C^{4}H^{3}PbO^{4}$.

Aqueous kinovin-magnesia does not precipitate *salts of iron* (Pelletier & Caventou).

Kinovin and Copper-oxide. — Aqueous kinovin-magnesia does not precipitate cupric salts (Pelletier & Caventou), or only strong solutions (Schnedermann). — Alcoholic kinovin precipitated with an aqueous solution of acetate of copper previously mixed with alcohol, forms a pale-blue compound, soluble in a large excess of alcoholic kinovin. It contains 10·77 p. c. of cupric oxide, but is paler in colour and less rich in copper, when the acetate of copper contains free acetic acid, or when the alcoholic solution is too weak (Schnedermann).

Two-thirds Kinovin-copper-oxide.			Schnedermann. *at* 100°. *mean.*
120 C	720	61·32	61·44
94 H	94	8·00	8·00
30 O	240	20·44	19·79
3 CuO	120	10·24	10·77
$2C^{60}H^{47}O^{15},3CuO$	1174	100·00	100·00

According to Schnedermann, $C^{38}H^{29}O^8$, CuO.

Kinovin and Silver-oxide.— According to Schnedermann, aqueous kinovin-magnesia precipitates silver salts, but according to Pelletier & Caventou it does not.— Kinovin-lime throws down from silver salts a white jelly (Winckler). By precipitating kinovin-ammonia with nitrate of silver a white precipitate is obtained, which turns brown-black on drying (Schnedermann).

The magnesia-compound precipitates cinchonine salts (Pelletier & Caventou).

Kinovin dissolves freely in *alcohol*, from which it is precipitated by *water* (Pelletier & Caventou). It is less freely soluble in *ether* (Winckler); dissolves also in *fixed and volatile oils*, especially when warm (Buchner).

Oxygen-nucleus $C^{48}H^{36}O^4$.

Dyslysin.

$$C^{48}H^{36}O^6 = C^{48}H^{36}O^4,O^2.$$

BERZELIUS. *Ann. Pharm.* 33, 139.
THEYER & SCHLOSSER. *Ann. Pharm.* 50, 244.
STRECKER. *Ann. Pharm.* 67, 29; 70, 149
MULDER. *Scheik. Onderz.* 5, 1.
HOPPE-SEYLER. *J. pr. Chem.* 89, 83.

The ultimate product obtained by the prolonged boiling of bile with hydrochloric acid, the cholic acid (choloïdic acid) formed by the breaking up of taurocholic and glycocholic acids, losing 4 atoms of water to form dyslysin.— Formed also by heating cholic acid to 195—200° (Hoppe-Seyler), to 300° (Strecker).

Bile, dissolved in a small quantity of water, is boiled for a day with strong hydrochloric acid; the resin thereby separated is treated with boiling water, which takes up only a small quantity if the action of the hydrochloric acid has been sufficiently prolonged; the residue is boiled with absolute alcohol; and the precipitate which forms on cooling is added to the undissolved portion. A further quantity of dyslysin may be obtained by evaporating the wash-waters and alcohol to dryness, and again boiling the residue with hydrochloric acid. The whole of the dyslysin thus obtained is dissolved in ether, and the solution is filtered and evaporated (Theyer & Schlosser).—Strecker boils glycocholic acid with hydrochloric acid, until the fluid resin first formed becomes hard and friable, exhausts it with boiling water and alcohol, dissolves in ether, and precipitates with alcohol.—When the mass obtained by heating cholic acid to 200° is powdered and exhausted with soda-ley, dyslysin remains, and may be purified by washing with water and alcohol (Hoppe-Seyler).

Properties.—White earthy mass (Berzelius), often coloured yellow or grey. Tasteless. Melts at 140° (Theyer & Schlosser).

		Theyer and Schlosser.		Strecker.		Mulder.	
48 C	288	77·41	77 73	77·45	77 33	77·00	77 01
36 H	36	9 68	9 56	9·60	9·66	9 33	9 55
6 O	48	12 91	12 71	12 95	13 01	13 67	13·41
$C^{48}H^{36}O^{6}$	372	100 00	100 00	100 00	100 00	100·00	100 00

According to Mulder, who distinguishes several varieties of dyslysin, the formula is $C^{50}H^{36}O^{6} + \frac{1}{2}$ aq. According to Theyer & Schlosser, it is $C^{60}H^{46}O^{7}$.

Dyslysin *burns* with a smoky flame, leaving a cinder difficult of combustion (Theyer & Schlosser).—By boiling with alcoholic *potash*, it is converted into cholate of potash (Hoppe-Seyler). Strecker obtained choloidic acid.

Dyslysin is insoluble in boiling *water*, and in *hydrochloric acid*, *aqueous ammonia*, and *potash*, and *acetic acid*. It dissolves slightly in boiling *alcohol* and freely in *ether* (Strecker, Theyer & Schlosser).

Primary Nucleus $C^{48}H^{44}$; *Oxygen-nucleus* $C^{48}H^{38}O^{6}$.

Aescigenin.

$$C^{48}H^{38}O^{8} = C^{48}H^{38}O^{6},O^{2}.$$

ROCHLEDER. *Wien. Akad. Ber.* 45, 675; *J. pr. Chem.* 87, 26; *Chem. Centr.* 1863, 17 and 33; *Kopp's Jahresber.* 1862, 489; further *J. pr. Chem.* 141, 418.

Obtained from argyraescin and aphrodaescin, either (*a*) by decomposing these bodies with hydrochloric acid, and treating the products with alcoholic potash; or (*b*) by the action of hydrochloric acid gas on alcoholic aescinic acid or alcoholic telaescin, both of which are formed from argyraescin or aphrodraescin.

Hydrochloric gas is passed into boiling alcoholic telaescin, until the yellow solution acquires a red colour and a green fluorescence; the aescigenin thereby formed, together with a yellow resin, is precipitated by water, and purified by dissolving it in alcoholic potash and reprecipitating with water. On boiling this precipitate with small quantities of alcohol, it dissolves, with the exception of a sticky substance. The solution on addition of water deposits at first coloured aescigenin, after the removal of which, more water throws down a purer product.

White or faint-yellow powder, appearing indistinctly crystalline under the microscope.

			Rochleder.		
			a.	b.	c.
48 C	288	73·85	73·74	72·31	73·43
38 H	38	9·74	9·91	10 08	10·12
8 O.	64	16·41	16·35	17 61	16·45
$C^{48}H^{36}O^8$	390	100 00	100·00	100·00	100 00

a was dried at 130° ; *b*, dried at 100°, retains an atom of water ; *c* is a more recent analysis. Rochleder now assigns to aescigenin the formula $C^{24}H^{20}O^4$, which requires 73·47 p. c. C., 10 20 H., and 16·33 O. (see page 43).*

Aescigenin dissolves in oil of *vitriol*, forming a yellow, or in presence of sugar a blood-red solution. — With *chloride of acetyl* it forms biacetaescigenin.

It is insoluble in *water* and aqueous *alkalis*, but easily soluble in *alcohol*.

Conjugated Compounds of Aescigenin.

a. Biacetaescigenin.

$$C^{56}H^{44}O^{14} = C^{48}H^{38}O^8,2C^4H^3O^3.$$

ROCHLEDER. *J. pr. Chem.* 87, 27 ; 101, 418.

Powdered aescigenin, digested with a large quantity of chloride of acetyl, becomes warm, evolves hydrochloric acid gas, and dissolves to a yellow liquid having a green fluorescence. On evaporating from the solution the excess of chloride of acetyl, there remains an amorphous residue, which is dissolved in alcohol and precipitated with water.

Biacetaescigenin forms a pale-yellow amorphous powder, melting at 100° to a resin, which is brittle and friable after cooling. — It loses a little acetic acid on prolonged heating to 100°.

			Rochleder.
	at 100°.		mean.
56 C	336	68·29	68·33
44 H.	44	8·94	8 83
14 O	112	22 77	22·84
$C^{18}H^{38}O^8,2C^4H^3O^3$	492	100·00	100·00

According to the new formula of aescigenin, that of the biacetate is $C^{32}H^{24}O^8 = C^{24}H^{18}(C^4H^3O^2)^2O^4$, requiring 68 57 p. c. C., 8·57 H., and 22·86 O.

b. Summary of the bodies obtained from the Seeds of the Horse-Chestnut.

The substances argyraescin and aphrodaescin, found in the seeds of horse-chestnut, are broken up by the action of acids and alkalis, ultimately yielding aescigenin, sugar, propionic or butyric acid, and, as Rochleder believes, mannitan :

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* According to this formula, the proper place of aescigenin and its derivatives would be in vol. xv.

$C^{108}H^{86}O^{18} + 12HO = C^{48}H^{38}O^{8} + 2C^{12}H^{12}O^{10} + 2C^{12}H^{12}O^{12} + 2C^{6}H^{6}O^{4}$.
Argyraescin. Aescigenin. Mannitan. Sugar. Propionic acid.

$C^{104}H^{84}O^{46} + 10HO = C^{48}H^{38}O^{8} + 2C^{12}H^{12}O^{10} + 2C^{12}H^{12}O^{12} + C^{8}H^{8}O^{4}$.
Aphrodaescin. Aescigenin. Mannitan. Sugar. Butyric acid.

The following intermediate compounds are also formed by the combination of aescigenin with one or more of the other products of decomposition, the differences in the compounds depending upon the nature or the intensity of the action of the decomposing agent.

If P denote an atom of propionic acid, B an atom of butyric acid, M an atom of mannitan ($C^{12}H^{12}O^{10}$), S an atom of sugar ($C^{12}H^{12}O^{12}$), and Ae an atom of aescigenin, the relations of these intermediate bodies may be expressed thus:

1. Ae + 2P = $C^{60}H^{50}O^{16}$ (*Bipropaescigenin*).—Obtained on one occasion by treating argyraescin with hydrochloric acid and alcohol, and precipitating the solution with water.

	at 100°.		Rochleder.
60 C	360	66·92	66·74
50 H	50	9·29	9·34
16 O	128	23·79	23·92
$C^{60}H^{50}O^{16}$	538	100·00	100·00

2. Ae + M − 3HO = $C^{60}H^{47}O^{15}$ (*Aescigenitan*).—This body was precipitated by water from a solution obtained by treating argyraescin with potash-ley, precipitating with sulphuric acid, dissolving the precipitate in alcohol, and treating the solution for a short time with hydrochloric acid gas.

	at 120°.		Rochleder.
60 C	360	68·31	68·46
47 H	47	8·91	8·92
15 O	120	22·78	22·62
$C^{60}H^{47}O^{15}$	527	100·00	100·00

3. Ae + 2M − 3HO = $C^{72}H^{59}O^{25}$ (*Telaescin*).—Obtained from argyraescin or aphrodaescin by the action of caustic potash and hydrochloric acid.

	Dried at 110° *in a vacuum.*		Schwarz.
72 C	432	62·52	62·37
59 H	59	8·54	8·51
25 O	200	28·94	29·12
$C^{72}H^{59}O^{25}$	691	100·00	100·00

	at 100°.		Kavalier.
72 C	432	60·17	60·02
62 H	62	8·64	8·62
28 O	224	31·19	31·36
$C^{72}H^{59}O^{25},3HO$	718	100·00	100·00

Rochleder now assigns to this compound the formula $C^{36}H^{30}O^{14}$, requiring 60·34 p. c. C., 8·38 H., and 31·28 O (p. 43).

4. Ae + M + B − 3HO = $C^{68}H^{55}O^{19}$ (*Aphrodaescetin*).—This body

was obtained by heating aphrodescin-baryta for some time with alcohol and hydrochloric acid, and precipitating with water.

	at 130°.		Rochleder.
68 C	408	66·34	66·32
55 H	55	8·94	9·19
19 O	152	24·72	24·49
$C^{68}H^{55}O^{19}$	615	100·00	100·00

5. Ae + 2M + 2P − 12HO = $C^{84}H^{62}O^{24}$ (*Argyraescetin*). — Obtained by heating argyraescin with acids. See below.

6. Ae + 2M + S − 4HO = $C^{84}H^{70}O^{36}$ (*Telaesglucin*). — *a.* Obtained on one occasion by heating crystallised aescinate of potash with weak hydrochloric acid for six hours over the water-bath. — *b.* This body is obtained in the form of a precipitate by warming the aqueous extract of ground horse-chestnuts with hydrochloric acid, boiling the precipitate with alcohol, filtering, boiling the filtrate with excess of baryta-water, filtering the hot liquid from the precipitate, dissolving the latter in hot water, filtering when the solution has cooled to 30°, and mixing the filtrate with hydrochloric acid.

	at 100°.		Kavalier. *a.*
84 C	504	58·47	58·55
70 H	70	8·12	8·34
36 O	288	33·41	33·11
$C^{84}H^{70}O^{36}$	862	100·00	100·00

	Dried in a vacuum.		Schwarz. (*mean.*) *b.*
84 C	504	56·12	56·22
74 H	74	8·24	8·19
40 O	320	35·64	35·59
$C^{84}H^{70}O^{36},4HO$	898	100·00	100·00

7. Ae + 2M + 2S − 6HO = $C^{96}H^{80}O^{46}$ (*Aescinic acid*). — Produced by heating argyraescin or aphrodaescin with strong aqueous alkalis, in the former case together with propionic acid, in the latter with butyric acid. See below.

8. Ae + 2M + 2S + P − 10HO = $C^{102}H^{82}O^{46}$ (*Propaescinic acid*). Obtained, like aescinic acid, as an intermediate product of the limited action of alkalis on argyraescin. See below.

c. Argyraescetin.

$$C^{84}H^{62}O^{24} = C^{48}H^{32}O^{2},2C^{12}H^{10}O^{8},2C^{6}H^{6}O^{3}.$$

ROCHLEDER. *Wien. Acad. Ber.* 45. 676; *J. pr. Chem.* 87, 6; 101. 417.

Formation. See above.

Hydrochloric acid gas is passed into alcoholic argyraescin; the liquid when cool is precipitated with water, and the pale-yellow flocks thus obtained are collected, washed, and dissolved in alcohol. From this solution water throws down first yellowish, afterwards white argyraescetin, the latter of which only is collected. After washing with water it is dried in a vacuum over oil of vitriol, and afterwards at 100° — 120°.

White, chalk-like amorphous powder, electric when rubbed, and melting to a thick oil when heated.

Dried at 100°—120°.			Rochleder. *mean.*
84 C	504	66·49	66·48
62 H	62	8·18	8·22
24 O	192	25·33	25·30
$C^{84}H^{62}O^{24}$	758	100·00	100·00

Rochleder's new formula for this compound is $C^{12}H^{30}O^{12}$, requiring 66·67 p. c. C., 7·94 H., and 25·39 O. (p. 43).

Argyraescetin when strongly heated turns brown, emits an odour of incense, and burns with a luminous smoky flame.

Combinations. — *With Water.* — Argyraescetin dried in a vacuum over oil of vitriol retains 7 atoms, that dried at 100° retains 3 atoms of water (Rochleder).

Dried at 100°.			Kavalier.
84 C	504	64·20	63·98
65 H	65	8·28	8·66
27 O	216	27·52	27·36
$C^{84}H^{62}O^{24},3HO$	785	100·00	100·00

Dried over oil of vitriol.			Schwarz. *mean.*
84 C	504	61·39	61·25
69 H	69	8·41	8·48
31 O	248	30·20	30·27
$C^{84}H^{62}O^{24},7HO$	821	100·00	100·00

Argyraescetin is insoluble in water, but easily soluble in *alcohol.*

d. Aescinic Acid.

$$C^{96}H^{80}O^{46} = C^{48}H^{36}O^{6},2C^{12}H^{12}O^{10},2C^{12}H^{10}O^{10}.$$

ROCHLEDER. *Wien. Acad. Ber.* 45, 675; *J. pr. Chem.* 87, 16; 4, 417.

Source. In the cotyledons of the horse-chestnut.

Formation. Page 34.

Preparation. 1. Powdered horse-chestnuts are freed from the greater part of their fat, and the residue is boiled with alcohol of 40°. The decoction deposits, on cooling, a small quantity of aescinic acid, amounting to 0·6 grm. from 8 pounds of chestnuts.

2. *From the Alcoholic extract of the Cotyledons.* To prepare this extract, fresh ripe horse-chestnuts freed from the brown skins and embryos, are comminuted and digested for a few days with alcohol of 35° Bm. in the cold. The extract is decanted and replaced once or twice by fresh alcohol, and the mixed tinctures are distilled until the residue has the consistence of honey. After standing in a warm place for some days, a layer of fat collects on the surface, on removing which the alcoholic extract remains as a brown mass. — Before proceeding to the further treatment of the extract, the sugar contained in it may be removed by fermentation, or by evaporating the extract to an unctuous consistence and kneading it with absolute alcohol.

a. An aqueous solution of the above extract, after being freed from the alcohol taken up in the process of kneading, is heated with potash-ley till it solidifies to a jelly from separation of aescinate of potash. It is then boiled with water and filtered, and the salt which crystallises on cooling is washed and decomposed with an acid. — *b.* The fermented solution of the extract, after precipitation with neutral acetate of lead, is precipitated with the basic acetate; the precipitate is decomposed with hydrosulphuric acid under weak spirit; the filtrate is evaporated to dryness; and the residue is boiled with potash-ley and a little alcohol. The aescinate of potash thereby separated is heated with alcoholic acetic acid and mixed with water, whereupon aescinic acid is deposited.

Aescinic acid is also obtained in the preparation of argyraescin.

Properties. Amorphous colourless mass, easily triturable to a white powder. The acid, dried at 100° and afterwards boiled with a quantity of alcohol of 40° B. insufficient to dissolve it, is converted into a crystalline powder: the solution likewise deposits crystalline acid on evaporation. — The acid dried at 115° loses ½ atom of water at 130° (by calc. 0·44 p. c.).

			Rochleder, Schwarz, and Kavalier.				
			a.		*b.*	*c.*	*d.*
96 C	576	56·25	55·29	55·26	56·29	56·68	56·91
80 H	80	7·11	8·09	7·73	8 07	7 90	7·99
46 O . .	368	35·94	36·62	37·01	35·64	35·42	35·10
$C^{96}H^{80}O^{46}$ ...	1024	100·00	100·00	100·00	100·00	100·00	100·00

The analyses are given in mean numbers. — *d* was dried at 130° and had lost a little water between that temperature and 115°. Rochleder regards *a*, *b*, and *c* as aescinic acid containing different proportions of water. All three, however, were dried at 100° and at 115° by turns; whilst acid dried in a vacuum over oil of vitriol contained the same percentage of carbon as that dried at 115°. According to Rochleder, the above formula is correct for *b*, whereas *a* contains 2 atoms of water more, *c* 1 atom, and *d* 1½ atom less.

Rochleder now assigns to aescenic acid the formula $C^{48}H^{40}O^{24}$, which requires 55·38 p. c. C., 7 69 H., and 36·93 O.

Decompositions. Aescinic acid turns yellow when *heated* above 130°. — When heated with *hydrochloric acid* it breaks up, with formation of sugar, and a second body consisting of either telaescin, telaesglucin, or aescigenin.

The acid dissolves slightly in cold and more easily in hot *water*. The aqueous solution is converted into a jelly by caustic potash.

Aescinate of Potash. — White silky needles, sparingly soluble in water. The salt loses its easy solubility in warm alcohol by drying, even at ordinary temperatures.

			Rochleder.	
96 C	576	54·23	53·84	53·28
79 H	79	7·44	7·55	7·53
45 O	360	33·90	33 92	34 72
KO	47·1	4 43	4 69	4·47
$C^{96}H^{79}KO^{46}$	1062·1	100·00	100 00	100·00

	Schwarz and Kavalier.			
	b.	*c.*	*d.*	*e*
96 C	53 31	54·15	54·47	52·71
79 H.	7·60	7·67	7·59	7·49
45 O.	34·52	33·73	33 49	33 07
KO	4·57	4·45	4·45	6·73
$O^{96}H^{79}KO^{46}$	100·00	100 00	100·00	100 00

The analyses *a* to *d* are in mean numbers. — Rochleder gives the above formula for *c* [dried at 110° in a vacuum (?)], and considers the differences in the composition of *a*, *b*, and *d* to be due to varying amounts of water: *b* dried at 100°, is said to contain 2 at.; *a*, dried at 117°, 1 at. more; *d*, dried at 120°, 1 at. less than *c*. Rochleder's formula for *e* is 2 $C^{96}H^{79}KO^{46}$, KO, HO. — According to the new formula of aescinic acid, this potash salt consists of $C^{96}H^{79}O^{47}$,KO, or $C^{48}H^{39}KO^{24}$, $C^{48}H^{40}O^{24}$.

Aescinate of Baryta. — Obtained from the potash-salt and chloride of barium.

	Dried at 128°.		Rochleder.
96 C	576	48·93	48 99
80 H	80	6·80	7·00
46 O	368	31·26	31·21
2 BaO	153·2	13 01	12 80
$C^{96}H^{80}O^{46}$,2BaO	1177·2	100·00	100·00

The new formula is $C^{48}H^{39}BaO^{24}$, requiring 49 01 p. c. C., 6 64 H., 31·31 O., and 13·04 BaO.

Aescinate of Lead. — Obtained from solutions in weak spirit of the potash-salt and neutral acetate of lead. — White amorphous jelly.

	at 100°.		Kavalier.
288 C	1728	41·25	41·16
240 H	240	5·73	5 89
138 O	1104	26 35	26·66
10 PbO	1117·4	26 67	26·29
$3C^{96}H^{80}O^{46}$,10PbO	4189·4	100·00	100·00

Amorphous aescinic acid dissolves easily in *alcohol* when freshly precipitated, but not after drying. It is precipitated in the amorphous state from its alcoholic solution by *ether*.

e. Propaescinic acid.

$$C^{102}H^{82}O^{46} = C^{48}H^{36}O^{6},2C^{12}H^{10}O^{8},2C^{12}H^{10}O^{10},C^{6}H^{5}O^{3},HO.$$

ROCHLEDER. *Wien. Acad. Ber.* 45, 675; *J. pr. Chem.* 87, 9.

Not named by Rochleder. — Occurs in the cotyledons of the horse-chestnut. — For its formation see page 34.

When argyraescin is dissolved in potash-ley of sp. gr. 1·27, and the solution is heated over the water-bath until the jelly first formed is liquefied, the liquid, on cooling, solidifies to a crystalline pulp of propaescinate of potash. The crystals are purified by pressure and recrystallisation from hot alcohol. — The propaescinic acid obtained in the preparation of argyraescin is powdered and boiled with absolute alcohol, which dissolves it slowly and deposits brown flocks on cooling. These brown flocks are redissolved with the exception of a slight brown residue, in hot absolute alcohol, and the whole of the alcoholic liquids are precipitated with strongly cooled ether. The precipitate is washed with ether and purified by repeatedly dissolving it in alcohol and precipitating with ether.

	Dried at 130°.		Rochleder. *a.* *mean.*	*b.*
102 C	612	57·63	57·60	58·43
82 H	82	7·72	7·88	7·65
46 O	368	34·65	34·52	33·92
$C^{102}H^{82}O^{46}$	1062	100·00	100·00	100·00

Rochleder gives for *b* the formula $C^{102}H^{80}O^{44}$, containing two atoms of water less than the above (calc. 58·62 p. c. C, 7·66 H.).

Propaescinic acid is converted by heating with *alkalis* into aescinic acid, with elimination of propionic acid.

The *potash-salt* forms white microscopic crystals.

Baryta-salt. — Thrown down as a dense white precipitate on adding chloride of barium to a solution of the potash-salt in weak spirit.

	at 115°.		Rochleder. *mean*
102 C	612	43·58	43·43
86 H	86	6·12	6·03
50 O	400	28·48	28·55
4 BaO	306·4	21·82	21·99
$C^{102}H^{80}O^{46},4BaO - 6HO$	1404·4	100·00	100·00

f. Argyraescin.

$$C^{108}H^{86}O^{46} = C^{48}H^{36}O^{6},2C^{12}H^{10}O^{8},2C^{12}H^{10}O^{10},2C^{6}H^{5}O^{3}.$$

ROCHLEDER. *Wien. Acad. Ber.* 45, 675; *J. pr. Chem.* 87, 3; 101, 417.

According to Rochleder, Frémy's *saponin* (xvi, 84) from horse-chestnuts is to be regarded as aphrodaescin, whilst Frémy's crystalline bitter substance [*Acide esculique?* (Kr.) xv, 53] is argyraescin. Saponin does not occur in ripe horse-chestnuts.

Compare Rochleder's former views, xvi, 88 *a*. On capsulaescinic acid from horse-chestnuts see xvi, 151; on aesculin, xvi, 19; on fraxin, xvi, 279.

Source. In the cotyledons of the horse-chestnut, in small quantity in the ripe, and somewhat more abundantly in the fully formed but still unripe fruit.

Preparation. 1. From the alcoholic extract of the cotyledons (p. 36) The extract is shaken up with moist hydrate of alumina, left to stand for 12 hours, and filtered; the filtrate is heated with neutral acetate of lead over the water-bath; and the precipitate thereby formed is collected and dissolved in absolute alcohol. The solution, treated with hydrosulphuric acid, filtered, and evaporated, leaves an amorphous residue; and the sulphide of lead, digested with alcohol of 35° B. gives up argyraescin, which crystallises on evaporation. The solution of the lead-compound of argyraescin in absolute alcohol may also be mixed with a large quantity of water and decomposed by hydrosulphuric acid, as above.—The liquid precipitated by neutral acetate of lead gives with the basic acetate a precipitate which yields a little more argyraescin.

2. An extract of the cotyledons, prepared with hot alcohol of 35°, is precipitated with alcoholic neutral acetate of lead, and the resulting plaster-like precipitate is removed. The liquid is then precipitated with basic acetate of lead, and this second precipitate is also removed. The filtrate throws down, on addition of small quantities of water, a precipitate which is to be rejected so long as it cakes together, and collected only when it becomes flocculent. After washing with water, the precipitate is decomposed with hydrosulphuric acid under weak alcohol; the filtrate is precipitated afresh with basic acetate of lead and a large quantity of water; and the precipitate is again decomposed with hydrosulphuric acid under alcohol. In this way most of the yellow colouring matter is got rid of, and a filtrate is obtained which leaves amorphous argyraescin on evaporation in a vacuum.

Amongst Rochleder's other modes of preparation occur the following:—

a. An aqueous solution of the extract of horse-chestnuts yields with basic acetate of lead a precipitate of aphrodaescin, argyraescin, and propaescinic acid. On decomposing the precipitate with hydrosulphuric acid under alcohol, and evaporating the filtrate, the propaescinic acid is deposited on cooling, whilst aphrodaescin and argyraescin remain in solution.—When the precipitate produced by basic acetate of lead is dissolved in cold dilute acetic acid and filtered, and small quantities of alcohol are added, a jelly is thrown down, which when dissolved in alcohol, yields argyraescin-lead by precipitation with basic acetate of lead and water. The liquid filtered from the jelly gives with basic acetate of lead and a large quantity of water aphrodaescin-lead and propaescinate of lead, which may be separated as above.

b. Neutral acetate of lead throws down from an aqueous solution of the extract of horse-chestnuts chiefly citric acid; but if a little alcohol be added, the precipitate formed on warming contains also argyraescin and aphrodaescin, which dissolve on treating the precipitate with alcohol and acetic acid in succession, whilst citrate of lead remains undissolved. On one occasion the precipitate formed by neutral acetate of lead contained also argyraescin. — The filtrate from the precipitate formed by the neutral acetate gives with the basic acetate a precipitate of argyraescin, aphrodaescin, aescinic acid, and the colouring matter which yields quercetin with acids.

c. On mixing a solution of the extract in a large quantity of water with neutral acetate of lead, removing the precipitate, adding to the filtrate basic acetate of lead mixed with an equal volume of alcohol of 35° B., and washing the precipitate thereby formed with hot alcohol, the portion remaining undissolved (α) contains aphrodaescin-lead and the colouring matter which yields quercetin, whilst argyraescin, aphrodaescin, and propaescinic acid remain in solution, and may be precipitated by water (precipitate β). α is decomposed by hydrosulphuric acid under weak alcohol; the filtrate is evaporated; the residue is dissolved in water, and the solution shaken with crystals of hydrate of baryta, whereupon aphrodaescin-baryta is thrown down. — β is decomposed by hydrosulphuric acid under alcohol; and the filtrate is evaporated to crystallisation, whereupon the argyraescin separates. On evaporating the mother-liquor and mixing the residue with cold water, a little more argyraescin remains undissolved. If the solution be again evaporated, and the residue mixed with hot water, the solution becomes turbid and deposits propaescinic acid in the form of a jelly, whilst the filtrate yields aphrodaescin-baryta on addition of baryta.

Properties. See hydrated argyraescin. This body is rendered anhydrous by exposure to a temperature of 130° in a current of carbonic acid.

	Dried at 130°.		Rochleder. *mean.*
108 C	648	57·96	57·82
86 H	86	7·69	7·77
48 O	384	34·35	34·41
$C^{108}H^{86}O^{48}$	1118	100·00	100·00

Rochleder now represents argyraescin by the formula $C^{54}H^{42}O^{24}$, requiring 58·06 p. c. C., 7·53 H., and 34·41 O. (see p. 43).

Decompositions. 1. Argyraescin melts on platinum foil to an amorphous yellowish mass, which afterwards puffs up, emitting an odour of incense, burns with bright smoky flame, and leaves a dense charcoal. — 2. It dissolves in cold *oil of vitriol* with pale golden-yellow colour; on dropping water into the solution, so that it becomes hot, it turns blood-red, and on addition of a large quantity of water deposits greyish-green flocks, evolving at the same time an odour of fatty acids. — 3. When heated with *mineral acids*, it is resolved into argyraescetin and sugar. Hydrochloric acid gas passed into hot alcoholic argyraescin colours the liquid yellow, afterwards red by transmitted light, with green fluorescence, and quickly effects the splitting up into argyraescetin and sugar; but secondary products are apt to be formed. The aqueous solution becomes turbid and deposits flocks when warmed with hydrochloric acid, but for complete decomposition an exposure to a temperature of 100° for six or eight hours is necessary. 100 parts of the crystallised monohydrated argyraescin thus treated yield 31·78 parts, whilst 100 parts of the amorphous ter-hydrate yield 31·43 parts, of sugar (calc. for $C^{108}H^{86}O^{48} = C^{84}H^{62}O^{24} + 2C^{12}H^{12}O^{12}$ requires 31·94 and 31·44 parts).

4. A solution of argyraescin in aqueous *alkalis* (in which it dissolves abundantly) becomes thick and viscid on warming and solidifies to a colourless jelly, which when further heated again turns fluid. The products of the reaction are either 2 atoms of propionic acid and 1 atom of aescinic acid, or an intermediate product of 1 atom of propionic acid and 1 atom of propaescinic acid, according to the strength of the alkali employed and the duration of the action. Traces of butyric and formic acids are also produced.

Combinations. *With Water.*—a. *Monohydrated Argyraescin.*—Obtained from weak spirit in microscopic crystals, which under a magnifying power of 420 diameters, appear as transparent six-sided tables, and dry up to a silky pellicle on the filter. On evaporating a solution in water or in absolute alcohol, it remains in the form of a colourless transparent gum, which contains 1 atom of water after drying at 100°.

	Dried at 100°.		Rochleder. *mean.* *a.*	*b.*
108 C	648	57·50	57·37	57·38
87 H	87	7·72	8·04	7·92
49 O	392	34·78	34·59	34·70
$C^{108}H^{86}O^{48},HO$	1127	100·00	100·00	100·00

b. *Ter-hydrated?*—Amorphous argyraescin dried over oil of vitriol in a vacuum contains 56·54 p. c. carbon; ter-hydrated argyraescin contains by calculation 56·59 p. c.

c. *Aqueous solution.* Argyraescin dissolves with difficulty in water, forming a frothy solution.

Argyraescin dissolves in moderately strong *acetic acid.* It is precipitated from its solution in absolute *alcohol* by *ether*, in the form of a white slimy mass.

g. Aphrodaescin.

$$C^{104}H^{84}O^{46} = C^{48}H^{36}O^{6},2C^{12}H^{10}O^{8},2C^{12}H^{10}O^{10},C^{8}H^{7}O^{3},HO.$$

ROCHLEDER. *Wein. Acad. Ber.* 45, 675; *J. pr. Chem.* 87, 12; 101, 418.

Source. In the cotyledons of the horse-chestnut, more abundantly than argyraescin.

Preparation. (p. 39.) Obtained as aphrodaescin-baryta in the preparation of argyraescin. This body is washed with baryta-water, exposed to the air for some time, and boiled with alcohol of 40°. The alcoholic liquid is filtered while hot and mixed with water, and the alcohol is driven off, whereupon the compound again crystallises. The aphrodaescin-baryta is either decomposed with aqueous acetic acid, and the aphrodaescin thereby precipitated is washed and purified by dissolving it in absolute alcohol; or it is decomposed with alcoholic hydrochloric acid, and the aphrodaescin is purified by precipitating the alcoholic solution with ether. — It must be dried in a current of carbonic acid.

Properties. Colourless amorphous mass. The dust excites violent sneezing.

Dried at 120° *and* 130°.			Rochleder. *a.*	 *b.*
104 C	624	57·99	57·77	57·64
84 H	84	7·81	8·03	7 95
46 O	368	34 20	34·20	34·41
$C^{104}H^{84}O^{46}$	1076	100·00	100·00	100·00

Rochleder supposes *b* dried at 120° to contain 1 atom of water. The new formula for this compound is $C^{104}H^{83}O^{47} = C^{104}H^{82}O^{46} + HO$, requiring 57·62 p. c. C., 7·66 H., and 34·72 O. (p. 43).

Aphrodaescin heated with aqueous *alkalis* breaks up into butyric acid and aescinic acid:

$$C^{104}H^{84}O^{46} + 4HO = C^{96}H^{80}O^{46} + C^8H^8O^4.$$

The decomposition resembles that of argyraescin. — It deposits a flocculent jelly when heated with aqueous *hydrochloric acid.*

Aphrodaescin dissolves easily in *water*, forming a solution which froths strongly.

Baryta-salt. — Baryta-water throws down from aqueous aphrodaescin a precipitate which dissolves very slightly in excess of baryta-water. — White crystals, soluble in warm alcohol. The solution is precipitated by water. When boiled with a quantity of alcohol of 40° B., not sufficient for complete solution, the undissolved portion melts.

at 100°.		Rochleder. *mean.*	*at* 130°.		Rochleder. *mean.*
104 C	52·50	52·46	104 C	54 56	54·47
87 H	7·40	7·29	83 H	7 26	7·17
50 O	33·66	33·67	45 O	31·48	31·91
BaO	6 41	6·58	BaO	6 70	6·42
$C^{104}H^{83}C^{45}$,BaO,4HO	100 00	100·00	$C^{104}H^{83}O^{45}$,BaO	100·00	100 00

The new formula of this salt is $C^{104}H^{81}BaO^{46}$, or $C^{104}H^{81}O^{45}$,BaO.

Aphrodaescin dissolves in *alcohol* more easily than saponin.

¶ According to the most recent researches of Rochleder (*Wien. Acad. Ber.* 55, [2], 819; *J. pr. Chem.* 101, 415; abstr. *Kopp's Jahresb.* 1867, 750), the constituents of horse-chestnut seeds form a series analogous to the glycol series, and having for its first term a diatomic alcohol, *aesciglycol*, analogous to glycol, thus:

Glycol . . .	$C^4H^6O^4$	Aesciglycol	$C^{14}H^{10}O^4$
Glycolal . .	$C^4H^4O^4$	Aesciglycolal . . .	$C^{14}H^8O^4$
Glycollic acid .	$C^4H^4O^6$	Aesciglycollic acid .	$C^{14}H^8O^6$
Glyoxal	$C^4H^2O^4$	Aesciglyoxal . . .	$C^{14}H^6O^4$
Glyoxalic acid	$C^4H^2O^6$	Aesciglyoxalic acid . .	$C^{14}H^6O^6$
Oxalic acid	$C^4H^2O^8$	Aescioxalic acid . .	$C^{14}H^6O^8$

Aesciglycol itself is not known; but aescigenin, according to the new formula, $C^{24}H^{20}O^4$, assigned to it by Rochleder, is homologous with it. Aesculetin $C^{18}H^6O^8$ may be regarded as biformyl-aesciglyoxal, $C^{14}H^4(C^2HO^2)^2O^4$. Aesciglyoxalic acid occurs, combined with phloroglucin, as the tannin of the horse-chestnut; aesciglycollic acid is the product of the action of sodium amalgam on quercetin; aescioxalic acid is produced by the action of alkalis on aesculetin, as also is aescorcin, $C^{18}H^8O^8 = C^{14}H^6(C^2HO^2)^2O^4$.

The formula $C^{48}H^{38}O^8$, originally assigned by Rochleder to aescigenin, rendered it necessary to suppose that the formation of that compound and sugar from the glucosides, aescinic acid, argyraescin, and aphrodaescin, was accompanied by the production of mannitan (p. 33). This substance, however, was never actually obtained, and the new formulæ render the assumption of its formation superfluous, inasmuch as they afford a direct explanation of the resolution of these glucosides into aescigenin and sugar.

Argyraescin is resolved by acids in aqueous solution into sugar and argyraescetin; with potash into propionate and aescinate of potash:

$$C^{54}H^{42}O^{24} = C^{12}H^{12}O^{12} + C^{42}H^{30}O^{12}$$

Argyræscin. Sugar. Argyræscetin.

$$C^{54}H^{42}O^{24} + 2KHO^2 = C^6H^5KO^4 + C^{48}H^{39}KO^{24}$$

Argyræscin. Propionate. Aescinate.

Aescinic acid is resolved by acids into telaescin and sugar; and telaescin in alcoholic solution is decomposed by hydrochloric acid into aescigenin and sugar:

$$C^{48}H^{40}O^{24} + H^2O^2 = C^{36}H^{30}O^{14} + C^{12}H^{12}O^{12}$$

Aescinic acid. Telæscin. Sugar.

$$C^{36}H^{30}O^{14} + H^2O^2 = C^{24}H^{20}O^4 + C^{12}H^{12}O^{12}$$

Telæscin. Aescigenin.

Aescigenin, treated with chloride of acetyl, is converted into biacetate of aescigenin and hydrochloric acid:

$$C^{24}H^{20}O^4 + 2C^4H^3O^2Cl = 2HCl + C^{24}H^{18}(C^4H^3O^2)^2O^4.$$

Aphrodaescin is resolved by potash into butyric and aescinic acids:

$$C^{104}H^{82}O^{46} + 3KHO^2 = C^8H^7KO^4 + 2C^{48}H^{39}KO^{24}$$

Aphrodaescin. Butyrate. Aescinate.

The percentage composition of these several compounds calculated from the new formulæ differs but little from that given by the older formulæ (see the preceding pages).

The following compounds are obtained from æsculetin (xvi, 23).

h. Para-æsculetin.

ROCHLEDER. *J. pr. Chem.* 90, 433; 101, 424.

Æsculetin boiled with solution of bisulphite of soda is converted into this isomeric modification, which unites with the bisulphite; and on mixing the solution first with a little dilute sulphuric acid and then with alcohol, the compound $C^{18}H^{6}O^{8},NaHS^{2}O^{6} + HO$ is precipitated as a white crystalline mass. This compound decomposed with an alkaline carbonate yields paraæsculetin, as an aldehyde-like body, in indistinct crystals containing $C^{18}H^{6}O^{8},5HO$.

	Dried over oil of vitriol.		Rochleder.
18 C .	108	48·43	48 26
11 H ..	11	4 93	5 17
13 O ...	104	46·64	46 57
$C^{18}H^{6}O^{8},5HO$	223	100·00	100·00

Para-æsculetin is very soluble in *water*, sparingly soluble in *ether*, more easily in *alcohol*. Exposed in the moist state to *ammonia*-vapour, it is converted into æsorcein.

i. Aescioxalic Acid.

$C^{14}H^{6}O^{8}$.

ROCHLEDER. *J. pr. Chem.* 101, 121.

Produced, together with formic and oxalic acids, by the action of boiling concentrated potash-ley on æsculetin. The resulting solution, which is red at first, soon turns yellowish red, and at the edges dark green; if the air has access to the liquid, a small quantity of a black substance soluble in alcohol is formed at the same time. The mass supersaturated with sulphuric acid then yields to ether the above-mentioned acids, and the ethereal solution leaves on evaporation a brown mass very soluble in water, which reduces sulphate of silver, even in the cold, with formation of a silver speculum.

Aescioxalic acid is obtained in greater purity by heating æsculetin for several hours with baryta-water in an atmosphere of hydrogen, precipitating the baryta first with carbonic, then with dilute sulphuric acid, and evaporating the light brown filtrate over oil of vitriol. Aescioxalic acid then remains as a white finely crystalline mass, containing 1 at. water (10·4 p. c.), which is given off at 105°.

	Crystallised.		Rochleder.		*Crystallised.*		Rochleder.
14 C ...	84	48·84	48·79	$C^{14}H^{6}O^{8}$...	154	89·54	
8 H ...	8	4·65	4·64	2HO	18	10·46	10·3
10 O ...	80	46·51	46·57				
$C^{14}H^{6}O^{8},2HO$....	172	100·00	100·00		172	100·00	

Isomeric with protocatechuic acid which is sometimes formed simultaneously with it; distinguished from catechuic acid by the noncoloration and non-precipitation of its solution by ferrous sulphate. With ferric chloride it forms a red-brown solution, changing to purple-violet when mixed with carbonate of soda.

k. Aescorcein.

$C^{18}NH^7O^{10}$.

ROCHLEDER. *J. pr. Chem.* 101, 425.

Produced by the action of ammonia gas on moistened para-æsculetin, the white compound immediately turning red, then dirty-violet, and after a few minutes forming a sky-blue liquid, which when left over oil of vitriol gives off ammonia and turns red again. This red solution gave with neutral lead acetate a light blue precipitate; and on washing this precipitate with water, suspending it in a small quantity of water containing acetic acid, filtering the red solution from the undissolved substance, adding alcohol to the filtrate, rejecting the first portions of the resulting precipitate, then filtering again, and precipitating completely with alcohol, a lead-salt was obtained which when dried in a vacuum over oil of vitriol, yielded 18·29 p. c. C., 1·65 H. and 63·18 PbO, agreeing nearly with the formula $C^{54}N^3H^{24}O^{33},10PbO$ or $3(C^{18}NH^7O^{10},HO) + 10PbO$, which requires 18·32 p. c. C., 1·65 H., and 63·03 PbO. It gave off water at 100°. Another lead salt prepared in like manner and dried at 100°, yielded by analysis 11·11 p. c. C., 0·92 H., and 78·48 PbO, agreeing nearly with the formula $C^{18}NH^7O^{10},7PbO$, which requires 10·92 C., 0·71 H., and 78·87 PbO.

These results give for æscorcein the formula $C^{18}NH^7O^{10}$. Its formation is represented by the equation—

$$\underset{\text{Para-æsculetin.}}{C^{18}H^6O^8} + NH^3 + O^4 = \underset{\text{Aescorcein.}}{C^{18}NH^7O^{10}} + 2HO$$

It has the composition of orcein in which 2 at. H are replaced by 2 at. formyl, that is to say, $C^{14}NH^5(C^2HO^2)^2O^6$.

l. Aescorcin.

$C^{18}H^8O^8$.

ROCHLEDER. *J. pr. Chem.* 101, 427.

Formed by the action of sodium amalgam on æsculetin suspended in water in an atmosphere of carbonic acid:

$$C^{18}H^6O^8 + H^2 = C^{18}H^8O^8.$$

It is a white pulverulent body nearly insoluble in neutral and acid liquids, but dissolving in alkalis with green colour, changing to red in contact with the air.

	at 130°.		Rochleder.
18 C	108	60·00	60·00
8 H	8	4·44	4·30
8 O	64	35·56	35·70
$C^{18}H^{8}O^{8}$	180	100·00	100·00

By dry distillation æscorcin is almost wholly resolved into carbon and water. In contact with ammonia and air it is very quickly converted into æscorcein.

Aesculetin treated with sodium amalgam and hot water in contact with the air, yields a red liquid and two amorphous bodies not yet examined.

Primary Nucleus $C^{48}H^{46}$; *Oxygen-nucleus* $C^{48}H^{40}O^{6}$.

Cholic Acid.

$$C^{48}H^{40}O^{10} = C^{48}H^{40}O^{6},O^{4}.$$

DEMARÇAY. *Ann. Pharm.* 27, 274; *Ann. Chim. Phys.* 67, 177.
DUMAS AND PELOUZE. *Ann. Pharm.* 27, 292.
THEYER AND SCHLOSSER. *Ann. Pharm.* 50, 244.
v. GORUP-BESANEZ. *Ann. Pharm.* 59, 129.
STRECKER. *Ann. Pharm.* 65, 130; 67, 1; 70, 159.
HOPPE-SEYLER. *J. pr. Chem.* 89, 83, 257 and 281.

The *cholic acid* of Demarçay and Berzelius, not of Gmelin. The *cholalic acid* of Strecker. — Discovered by Demarçay.

Formation. 1. Cholic acid is formed, together with glycocoll, in the decomposition of glycocholic acid, and together with taurine in the decomposition of taurocholic acid. When the decomposition is effected by alkalis, a purer cholic acid is obtained than when the decomposition is brought about by acids or by putrefaction, the product in the latter case being a mixture of cholic acid and dyslysin (the choloïdic acid of some chemists, p. 53) — 2. Dyslysin heated with alkalis yields cholates (Berzelius. Hoppe-Seyler).

Preparation. 1. Aqueous glycocholate of soda is heated to boiling with an excess of caustic potash not sufficient to throw down the soda-salt, and maintained at that temperature (the water which evaporates being replaced) for 24 to 36 hours, or until the potash-salt at first precipitated in the amorphous state begins to assume a crystalline appearance. The liquid, when concentrated and left to cool, deposits cholate of potash, in the form of a crystalline mass, which is collected, pressed, dissolved in water, and mixed with hydrochloric acid, whereby cholic acid is precipitated as a viscid resin, becoming solid and friable after some time. It is obtained in crystals from its solution in ether-alcohol (Strecker).

When glycocholic acid is decomposed by boiling for 24 hours with an excess of saturated baryta-water, the glycocoll formed together with the cholic acid may also be recovered from the solution. The liquid is allowed to cool; the crystalline pulp is washed with a small quantity of boiling water, which dissolves chiefly baryta; and the residue is decomposed with hydrochloric acid. The mother-liquors and wash-waters, when treated with carbonic acid, deposit the excess of baryta, as carbonate, together with a little cholate of baryta, which may be decomposed by carbonate of ammonia. The cholate of ammonia thus formed, and the cholate of baryta of the other solutions, are decomposed by hydrochloric acid, whereupon cholic acid is precipitated, whilst hydrochlorate of glycocoll and chloride of barium remain in solution (Strecker).

2. Ox-gall is boiled with dilute potash-ley, with addition of sufficient water to retain the products in solution, for several days or so long as ammonia continues to be evolved. The liquid is then concentrated till the potash-salt is deposited in masses, which are removed, dissolved in water, and decomposed with dilute sulphuric acid. The precipitate thus obtained is freed from sulphuric acid by boiling repeatedly with fresh portions of water, whereby it is rendered hard, crystalline, and friable; after which it is washed with ether to remove colouring matter, dissolved in boiling alcohol, mixed with enough water to produce turbidity, and left to cool, whereupon cholic acid crystallises. The coloured crystals are purified by recrystallisation from alcohol, with addition of water (Theyer & Schlosser) or by exhaustion with a small quantity of ether (Strecker). Demarçay adopts a similar process.

When a mixture of glycocholate and taurocholate of soda is heated, first to 100° for 24 hours, and afterwards to 120° for an hour, with concentrated potash-ley in a sealed tube, and the contents of the tube are mixed, first with water and a few drops of ether, and then with hydrochloric acid, cholalic acid is deposited. After washing the product is quite pure, and corresponds in quantity with the calculated amount for the substances employed (Hoppe-Seyler).

If dyslysin be boiled for an hour with alcoholic potash, and the alcohol be afterwards driven off, cholate of potash is deposited in the form of an oil, which subsequently solidifies. Hydrochloric acid throws down the cholic acid from an aqueous solution of the salt (Hoppe-Seyler).

Gorup-Besanez found that bile allowed to putrefy at 12° to 15°, in contact with air, yielded cholic acid instead of the choloïdic acid formed at higher temperatures. The product was isolated by evaporating the decomposed bile, exhausting with absolute alcohol, evaporating the solution, treating the residue with ether, dissolving in water, precipitating with acetic acid, and crystallising.

Cholic acid thus obtained is either anhydrous, or combined with 2 or with 5 atoms of water.

Properties. Cholic acid which has not been treated with ether, and is consequently not quite free from fatty acids, crystallises in anhydrous, hard, permanent, four- or six-sided prisms with two oblique end-faces, both of which lie in the same zone with two of the side-faces. The crystals do not change at 135° in an air-bath, and are recovered unaltered from a solution in alcohol, in which they dissolve with difficulty. It exerts a dextrorotatory action on polarised light; $[\alpha]D$ (determined for Fraunhofer's line D) $= 50{\cdot}2°$. Has an acid reaction. Tastes bitter (Demarçay), sweetish, then pure bitter; the dust excites sneezing (Theyer and Schlosser).

The acids with two and with five atoms of water, both become anhydrous on drying, but at different temperatures (Strecker).

	Dried.		Strecker. *mean.*	Gorup-Besanez.	Theyer and Schlosser.
48 C	288	70·59	70·52	69·45	69·65
40 H	40	9·80	9·87	10·05	9·80
10 O	80	19·61	19·61	20·50	20·55
$C^{48}H^{40}O^{10}$	408	100·00	100 00	100·00	100·00

The acid analysed by Gorup-Besanez, and that of Theyer and Schlosser, probably contained some of the bi-hydrated acid, which gives off its water with difficulty (Strecker). — Theyer and Schlosser give the formula $C^{42}H^{33}O^{9}$.

Decompositions. 1. Dehydrated cholic acid melts at 195°, giving off 2·3 p. c. of water (1 atom = 2·21 p. c. HO), and forming a colourless liquid which, on cooling, solidifies to a mass resembling choloïdic acid (p. 53): above 200° it becomes thick, and about 300° turns brown and is converted into dyslysin, with elimination of 7·3 p. c. water: $C^{48}H^{40}O^{10} = C^{48}H^{36}O^{6} + 4HO$ (calc. 8·82 p. c. HO) (Strecker). See also p. 54. — 2. Cholic acid submitted to *dry distillation* yields an acid faintly yellow oil, which dissolves in ether and alkalis, and forms amorphous precipitates with metallic salts; a small quantity of charcoal is left behind (Strecker). — 3. Cholic acid *burns* with a very smoky flame, leaving charcoal (Demarçay). — 4. By boiling with strong *hydrochloric acid*, it is converted into choloidic acid, and ultimately into dyslysin (Strecker).

5. Cold *nitric acid* has no action on cholic acid, but the hot acid dissolves it with violent frothing and evolution of nitric oxide, forming a dark-yellow liquid, which after long-continued action contains cholesteric acid (xiii. 157), but no volatile fatty acid (Schlieper). See also choloïdic acid. — 6. Cholic acid, heated to 200° with *glycerin*, yields a mixture of glycerides (Hoppe-Seyler). — 7. Heated with *oil of vitriol* it behaves like glycocholic acid (p. 58) (Städeler); warmed with oil of vitriol and a little sugar-solution, it exhibits a violet-red colour (Strecker).

Combinations. — *With Water.* A. *With* 1 *atom of Water?* The salt with 2 atoms of water retains 1 atom at 100°, or gives it off with difficulty only at that temperature (Strecker).

	at 100°.		Strecker. *mean.*
48 C	288	69 06	68·97
41 H	41	9·83	9·83
11 O	88	21·11	21·20
$C^{48}H^{40}O^{10}$ + aq.	417	100·00	100·00

B. *With* 2 *atoms of Water.* — Obtained by precipitating the aqueous soda-salt with hydrochloric acid, in presence of ether, and setting aside for some days (Hoppe-Seyler). It crystallises from its alcoholic solution mixed with water in needles, and from ether in colourless transparent tables (Strecker). Right prismatic. Fig. 62 without *p*, but with the edge *u'* : *u* truncated by a face *t*. Four faces of the octohedron, which would together form a horizontal prism, are more developed than the other four, so that the crystals are terminated above, not with an octohedral summit, but with an edge, and exhibit an oblique prismatic character. The contiguous octohedral faces opposite this edge intersect at an angle of 71° 58′. The acute prismatic angle = 62° 15′ (Kopp).

The acid loses 2·4 p. c. water at 100° (1 at. = 2·11 p. c. HO), and 2·4 p. c. more at 140°; turns yellow at 145°, and melts at 145° to 150°, without undergoing decomposition (Strecker). It dissolves with difficulty in ether, but more easily in alcohol, the latter solution quickly depositing crystals containing 5 atoms of water (Hoppe-Seyler).

			Dumas and Peligot.	Strecker.
48 C	288	67·61	67·2	68·34
42 H	42	9·86	9·7	10 00
12 O	96	22·53	23·1	21·66
$C^{48}H^{40}O^{10}$ + 2aq.	426	100·00	100·0	100·00

C. *With* 5 *atoms of Water.* — Obtained by dissolving in alcohol the crystals deposited from ether, and evaporating (Hoppe-Seyler). Brittle, colourless glassy tetrahedrons, or quadratic octahedrons, which effloresce and become opaque in dry air. The crystals obtained from boiling alcohol belong to the square prismatic system. They are either octahedrons with the obtuse lateral summits truncated (fig. 29, but with the *q*-faces much smaller, so that the lateral edges of the octahedron are still partly developed), $e : e = 116° 14'$; $e : e'' = 96° 40'$; or they are the tetrahedrons derived from the octahedrons, in which the *q*-faces appear as truncations of the zig-zag edges. The angle between these edges = 63° 46′ (Kopp, *Ann. Pharm.* 67, 5). Kobell (*Ann. Pharm.* 59, 143) found the same octahedrons and determined the angles as approximately 117° and 95° 30′.

This acid loses at 100° the whole of its water, amounting on the average to 9·9 p. c (5 at. = 9·94 p. c. HO), and suffers no further change at 170° (Strecker). It rotates a ray of polarised light to the right, $[\alpha]D = 31·2°$ for the acid with 5 atoms of water (Hoppe-Seyler).

D. *Aqueous solution.* — The acid with 5 atoms of water dissolves in 750 parts of boiling, and in 4,000 parts of cold water (Strecker).

These solutions deposit microscopic pyramids and prisms with six faces, apparently inclined at equal angles, and terminated by end-faces at right angles to the longitudinal axis (Hoppe-Seyler).

Salts of Cholic Acid. — The acid neutralises bases, and decomposes carbonates with effervescence, forming salts soluble in alcohol but insoluble in ether; the salts of the alkalis dissolve also in water. The salts have a bitter and somewhat sweet taste: they produce a violet-red coloration with oil of vitriol and sugar (Strecker). The aqueous cholates of the alkalis are precipitated by chloride of sodium (Theyer and Schlosser). The stronger acids throw down from the salts amorphous cholic acid as a pasty precipitate, which is easily soluble in alcohol and ether, less freely soluble in water, and rapidly becomes crystalline.

Cholate of Ammonia. — The acid dissolves easily in dilute ammonia. On passing ammonia-gas into alcoholic cholic acid, and mixing the product with ether, needles or prisms are deposited, which lose ammonia on exposure to the air or on boiling, and leave an acid resin on evaporation (Strecker).

Cholate of Potash. — The alcoholic acid, neutralised with caustic potash and mixed with ether, deposits, on standing, needles of the potash-salt, which are likewise formed on evaporating the solution (Strecker). The salt is also formed by evaporating a solution of the acid to dryness with carbonate of potash, exhausting the residue with absolute alcohol, and evaporating to crystallisation (Hoppe-Seyler) After drying at 100° it does not undergo change at 150°. The aqueous solution leaves an amorphous varnish on spontaneous evaporation (Strecker). Exerts a right-handed action on polarised light; $[\alpha]D = 30·8°$ in alcoholic solution, and consequently $= 33·7°$ for the acid contained in the salt. In aqueous solutions the rotatory power depends on the concentration, and is greater in dilute than in strong solutions: it is also diminished by the addition of potash-ley (Hoppe-Seyler). The salt has a faintly alkaline reaction (Strecker).

			Strecker.	
	at 100°—150°.		*earlier.*	*later.*
48 C	288	64·56	63·94	64·63
39 H	39	8·74	8·76	8·76
9 O	72	16·14	16·78	16·20
KO	47·1	10·56	10·52	10·41
$C^{48}H^{39}KO^{10}$	446·1	100·00	100·00	100 00

The above salt, but no acid salt, is precipitated by ether from an alcoholic solution of the potash-salt mixed with excess of cholic acid (Strecker).

Cholate of Soda.—Precipitated in tufts of long fine needles on mixing an alcoholic solution of the salt with an equal volume of ether Has a pure bitter taste. Dissolves easily in water, alcohol, and acetic acid (Theyer and Schlosser).

The soda-salt exerts a right-handed action on polarised light: in the alcoholic solution $[\alpha]D = 31·4°$ for the salt, $= 33·1°$ for the acid contained in it. In aqueous solution the rotatory action is less, $[\alpha]D = 25·0°$, and varies with the strength when the solution contains less than 9 grammes in 100 cubic centimetres (Hoppe-Seyler).

	at 120°.		Theyer and Schlosser.
48 C	288	66·98	66·71
39 H	39	9·07	9·40
9 O	72	16·73	16·50
NaO	31	7·22	7·39
$C^{48}H^{39}NaO^{10}$	430	100·00	100·00

Cholate of Baryta.—Chloride of barium throws down a flocculent precipitate from concentrated aqueous solution of cholate of potash: solutions containing 3 p. c. or less of the potash-salt are not precipitated (Strecker). On dropping hot alcoholic cholic acid into boiling baryta-water, dense flocks of the baryta-salt are precipitated, which must be washed with warm water free from air (Theyer and Schlosser). A solution of cholic acid in excess of baryta-water is treated with (not too much) carbonic acid, then boiled and evaporated to crystallisation (Strecker).—Silky crystalline crusts soluble in 30 parts of cold and in 23 parts of boiling water, and more freely in alcohol, from which it crystallises (Strecker). The salt is precipitated by water from its solutions in alcohol and in acetic acid (Theyer and Schlosser). The aqueous and the alcoholic solutions are decomposed by prolonged treatment with carbonic acid, without yielding an acid salt (Strecker).

	at 100° *to* 120°.		Theyer and Schlosser. *mean.*	Strecker. *mean.*
48 C	288	60·58	59·58	60·07
39 H	39	8·20	8·72	8·26
9 O	72	15·15	13·74	15·59
BaO	76·4	16·07	17·96	16·08
$C^{48}H^{39}BaO^{10}$	475·4	100·00	100·00	100·00

Cholate of Lime. — Aqueous cholate of potash, containing 3 p. c. of cholic acid, forms, on addition of chloride of calcium, a thick paste, which is converted by ether into crystalline needles. The baryta-salt is likewise precipitated by chloride of calcium (Strecker). The precipitate thrown down by chloride of calcium from cholate of soda, dissolves in boiling alcohol, after washing with water, and on concentrating the solution and cooling, is deposited in the form of a dense white mass, which dries up to a very light powder. The salt is obtained also by boiling alcoholic cholic acid with hydrate of lime (Theyer and Schlosser). It dissolves very slightly in cold, but more easily in hot water (Strecker), and is soluble in alcohol and in acetic acid, from which it is precipitated by water (Theyer and Schlosser).

	at 100° to 120°.		Theyer and Schlosser.	Strecker.
48 C	288	67·45	66·16	
39 H	39	9·13	9·07	
9 O	72	16·86	17·41	
CaO	28	6·56	7·36	6 64
$C^{48}H^{39}CaO^{10}$	427	100·00	100·00	

Cholate of soda does not precipitate *sulphate of magnesia* (Theyer and Schlosser); it throws down semi-crystalline flocks from *salts of manganese* (Strecker). The *zinc-salt* is insoluble (Demarçay).

Cholate of Lead. — *Four-fifths?* — Obtained by precipitating neutral aqueous cholate of ammonia with basic acetate of lead, dissolving the washed precipitate in boiling alcohol, and evaporating. — Crystalline warts, soluble in acetic acid and in alcohol, from which they are precipitated by water (Theyer and Schlosser).

	at 120°.		Theyer & Schlosser. *mean.*
192 C	1152	53·21	52·34
157 H	157	7·25	7·18
37 O	296	13·67	14 29
5 PbO	560	25·87	26·19
$4(C^{48}H^{39}PbO^{10}),PbO,HO$	2165	100·00	100·00

Cholate of soda throws down from *ferric chloride* a pale-yellow, from *cupric acetate* and *sulphate* a blue, from *mercurous nitrate* and *mercuric chloride* a white precipitate, soluble in alcohol.

Cholate of Silver. — A. *Neutral.* — Precipitated from aqueous cholate of soda by nitrate of silver, as a white jelly, which dries up to brown lumps, easily soluble in alcohol and in acetic acid, and precipitated therefrom by water (Theyer and Schlosser). The salt is deposited in the crystalline state from its solution in boiling water. The aqueous solution, mixed with acetic acid, deposits a small quantity of crystals of cholic acid (Strecker).

	at 100°.		Theyer and Schlosser.	Gorup-Besanez.
48 C	288	55·92	56·38	
39 H	39	7·57	7·73	
9 O	72	13·98	14·25	
AgO	116	22·53	21·64	20·49
$C^{48}H^{39}AgO^{10}$	515	100·00	100·00	

B. *Acid?* — Dense white flocks thrown down by nitrate of silver from cholate of ammonia, in presence of a little free nitric acid. The salt dissolves in alcohol and in acetic acid, and is precipitated from the solutions by water (Theyer and Schlosser).

	at 100°.		Theyer & Schlosser. *mean.*
96 C	576	62·67	64·00
79 H	79	8·59	8·85
19 O	152	16·54	17·38
AgO	112	12·20	9·77
$C^{48}H^{39}AgO^{10} + C^{48}H^{40}O^{10}$	919	100·00	100·00

Probably a mixture containing free cholic acid (Kr.).

The acid with 5 atoms of water dissolves slowly but abundantly in boiling *alcohol:* 1000 parts of 70 p.c. alcohol retain in solution, after cooling, 48 parts of the anhydrous acid. Water turns the alcoholic solution milky, and throws down crystals. — The anhydrous acid dissolves in 27 parts of *ether* (Strecker). — The acid dissolves in 22 parts of *glycerin* at 30°, forming a solution from which it is not deposited even on standing for months; the addition of a drop of hydrochloric or phosphoric acid renders the solution turbid, from the separation of oily drops, which solidify in 24 hours to crystals of cholic acid (Beneke, *Studien über Galle*, 85).

Appendix to Cholic Acid.

Choloïdic Acid.

$$C^{96}H^{78}O^{18} = C^{48}H^{39}O^{9},C^{48}H^{39}O^{9}.$$

The *bile-resin* of Thénard and Gmelin. According to Hoppe-Seyler it is a mixture of cholic acid and dyslysin (see below). Mulder (*Scheik. Onderz*, 5, 13) described choloïdic acid as a mixture of fellic and cholinic acids, the former having the composition of cholic acid, and the latter containing 2 atoms of water less.

Formation. 1. By boiling bile with phosphoric, sulphuric, or hydrochloric acid (Demarçay), or with oxalic acid (Theyer and Schlosser). — 2. By heating cholic acid to 195°, or by boiling it with acids (Strecker). — 3. By the putrefaction of bile (Gorup-Besanez).

Ox-gall, purified by dissolving it in alcohol and evaporating to dryness, is dissolved in 12 to 15 parts of water, and boiled for 3 or 4 hours with excess of hydrochloric acid. After cooling, the supernatant liquid is decanted, and the deposit is freed from most of the hydrochloric acid by means of a little water, triturated, washed, dissolved in a small quantity of alcohol, shaken with ether to remove cholesterin and fatty acids, and evaporated (Demarçay).

Theyer and Schlosser investigated the brown resin produced by digesting a strong solution of bile for some days with excess of oxalic acid, and purified by boiling with water, or by dissolving in caustic potash and precipitating with sulphuric acid. Inasmuch as the product thus obtained may be contaminated with glycocholonic acid, it is better first to convert the bile-acids into cholic acid, from which the choloïdic acid may be obtained by the action of acids or of heat. In the latter case the choloidic acid may be freed from unaltered cholic acid by precipitating its ammoniacal solution with chloride of barium, the cholic acid then remaining in solution (Strecker, *Handworterbuch*, [2] 2, 2, 1188).

Strecker's choloïdic acid was obtained by boiling glycocholic acid with hydrochloric acid, and was purified by precipitating its alcoholic solution with ether, re-dissolving in alcohol, and precipitating with water.

Ox-gall left exposed to the air for two or three weeks, at the temperature of 31° to 37°, undergoes spontaneous decomposition, attended with development of fungi and vibrios. When the product is inspissated and exhausted with absolute alcohol, taurine and altered mucus remain undissolved. The alcoholic solution is decolorised with animal charcoal, concentrated, freed from fats and from colouring and odorous matters by means of ether, and diluted with alcohol, whereupon a small quantity of crystalline needles (according to Gorup-Besanez, of margaric acid, but more probably of cholonic acid) is deposited. The solution is then evaporated and the residue dissolved in water and precipitated with acetic acid. Choloïdic acid separates in the form of a plaster, which is to be kneaded with water till it becomes hard and pulverulent and free from ammonia and potash, after which it is to be dried, dissolved in alcohol, decolorised with animal charcoal, and the solution evaporated (Gorup-Besanez).

Properties. Solid white or yellow friable mass, inodorous and very bitter. Melts below 100° (Theyer & Schlosser), above 100° (Gorup-Besanez). Melts completely at 150°, but softens at the temperature of boiling water (Demarçay). Has an acid reaction (Demarçay). Free from nitrogen (Demarçay; Theyer & Schlosser) and from sulphur (Gorup-Besanez).

	at 100°—120°.		Demarçay.	Pelouze & Dumas.	Theyer & Schlosser.	
					a.	*b.*
48 C	288	72·18	72·01	72·29	71·74	71·86
39 H	39	9·77	9·52	9·70	9·58	10·13
9 O	72	18·05	18·47	18·01	18·68	18·01
$C^{48}H^{39}O^{9}$	399	100·00	100·00	100·00	100·00	100·00

	Strecker.	Gorup-Besanez.		
		a.	*b.*	*c.*
C	71·95	72·74	72·97	72·37
H	9 79	9·82	10 16	10·12
O	18·26	17·44	16·87	17·51
	100·00	100 00	100·00	100·00

b was precipitated from an alkaline solution by sulphuric acid (Theyer & Schlosser), *c* by acetic acid (Gorup-Besanez). — Mulder's cholinic and fellic acids, containing respectively 72·41 C., 10·07 H., and 71·80 C., 9 80 H., probably belong to this place.

Earlier formulæ · $C^{37}H^{30}O^6$ (Demarçay), $C^{38}H^{30}O^7$ (Dumas & Pelouze), $C^{60}H^{50}O^{11}$ (Theyer and Schlosser). Gerhardt (*Compt. Chim.* 1, 48) supposes the above formula of Strecker's to contain an atom of water. — Hoppe-Seyler regards the choloidic acid of Demarçay and of Theyer & Schlosser [who, however, found their acid to be free from nitrogen (Kr.)] as a mixture of cholic acid, dyslysin, glycocholonic acid, and undecomposed glycocholic and taurocholic acids; and that of Strecker as a mixture of dyslysin and cholic acid. His view is founded upon the following experiments, which, however, do not appear to contradict the view that choloidic acid may be a body allied to the anhydrides or to the condensed acids (Kr.).

a. When crystallised bile is boiled for some hours with hydrochloric acid, the resins formed always contain nitrogen. On precipitating their solution in soda-ley with chloride of barium, boiling water takes up from the precipitate a large quantity of baryta-salt, which does not crystallise on evaporation, but when shaken with ether and hydrochloric acid, deposits a soft fatty mass, in which crystals of cholic acid gradually form under alcohol.

b. The mass obtained by heating cholic acid to 200°, or by melting the acid at 195°, already contains dyslysin, together with undecomposed cholic acid. On treating the cooled mass with soda-ley, the dyslysin remains behind, whilst the alkaline solution deposits cholic acid with 5 atoms of water on addition of hydrochloric acid.

c. Concentrated aqueous cholic acid dissolves a large quantity of dyslysin, which is partially precipitated by the addition of water. Aqueous cholate of soda also dissolves dyslysin, which is precipitated from the solution by carbonic acid: on mixing the clear solution with hydrochloric acid, a precipitate is thrown down, of which warm alcohol dissolves a part, leaving the rest in the form of an oil. This oil, as well as the residue left on evaporating the alcoholic solution, exhibits the properties of choloidic acid (Hoppe-Seyler).

Decompositions. Choloïdic acid, subjected to prolonged boiling with *hydrochloric acid*, becomes insoluble in cold and ultimately even in boiling alcohol, being converted into dyslysin. Intermediate products are formed, consisting of resins, which swell up in ammonia-water without dissolving (Strecker). — The acid does not appear to be altered by boiling for several days with *potash-ley* (Theyer & Schlosser). See above.

Choloïdic acid is violently attacked by moderately dilute *nitric acid*, frothing up from liberation of nitric oxide, and being converted into a soft resin and partially dissolved. When it is boiled as long as any action occurs, with addition of more nitric acid if necessary, volatile products are formed, including acetic, valerianic, caprylic, capric, and probably butyric acids, together with a heavy oil, which is resolved by alkalis into nitrocholic acid and cholacrol (ix, 503): amongst the non-volatile products are cholesteric (xiii, 157), oxalic, and choloïdanic acids (xvi, 412) (Redtenbacher, *Ann. Pharm.* 57, 145). — The acid is for the most part converted into dyslysin when boiled with *bichromate of potash* and *sulphuric acid;* an odorous distillate, however, is obtained, on the surface of which float flocks or oily drops, which may be separated by shaking the distillate with ether. These flocks are fusible and volatile, soluble in aqueous alkalis, and precipitated therefrom by acids: they yield a white curdy silver-salt, containing 64·72 p. c. of silver, agreeing in composition with collinate of silver, $C^{12}H^3AgO^4,AgO$ (Fröhde, *Krit. Zeitschr.* 7, 469).

Combinations. — Choloïdic acid is nearly insoluble in *water.* — It neutralises bases, and expels carbonic acid from carbonates on warming. The salts have a pure bitter taste: those of the alkalis are soluble in water and in alcohol, but not in ether; their aqueous solutions are decomposed by carbonic acid, and precipitated by chloride of ammonium and by caustic alkalis and their carbonates. The salts of the earths and metals, obtained as sticky masses by double decomposition, are soluble in alcohol but insoluble in water (Strecker). Mineral acids precipitate choloidic acid from its salts in its original state (Demarçay). According to Hoppe-Seyler, the salts are identical with those of cholic acid.

The solution of the acid in aqueous *ammonia* turns acid on boiling.

Baryta-salt.—An alcoholic solution of choloïdic acid is mixed with excess of baryta-water and evaporated, and the residue is exhausted with cold alcohol, which leaves, on evaporation, an amorphous mass nearly insoluble in water (Strecker).

	at 120°.		Strecker.
48 C	288	60·58	60·40
39 H	39	8·20	8·32
9 O	72	15·15	15·21
BaO	76·4	16·07	16·07
$C^{48}H^{39}BaO^{10}$	475·1	100·00	100·00

Lead-salt.—Obtained by precipitating aqueous choloïdate of potash with basic acetate of lead, washing the dense white precipitate with water, dissolving in alcohol, and leaving the solution to evaporate (Theyer & Schlosser).

Calculation according to Strecker.			Theyer & Schlosser. *at* 120°.
48 C	288	50·84	50·37
39 H	39	6·88	6·80
9 O	72	12·73	13·51
$1\frac{1}{2}PbO$	167·4	29·55	29·32
$C^{48}H^{39}O^9,1\frac{1}{2}PbO$	566·4	100·00	100·00

Silver-salt.—The ammonia-salt throws down from nitrate of silver a jelly, which dries up to yellowish-brown lumps. The powder is reddish-brown. It dissolves with difficulty in alcohol (Theyer & Schlosser).

	at 100°.		Theyer & Schlosser
48 C	288	55·92	58·65
39 H	39	7·57	8·11
9 O	72	13·99	13·90
AgO	116	22·52	19·34
	515	100·00	100·00

Gorup-Besanez found 16·49 p. c. AgO

The acid dissolves easily in *alcohol*, and is precipitated in the form of a resin by water.—It is slightly soluble in *ether* (Strecker).

Conjugated Compounds of Cholic Acid.

Cholate of Methyl.

$$C^{56}H^{42}O^{10} = C^{2}H^{3}O,C^{48}H^{39}O^{9}.$$

HOPPE-SEYLER. *J. pr. Chem.* 89, 272.

Methyl-ether of cholalic acid.—Iodide of methyl acts rapidly on cholate of silver at a gentle heat, with formation of cholate of methyl, which is purified by treating the product with potash-ley and with ether.

Long, colourless, hard, four-sided prisms, terminated by two end-faces inclined at a very obtuse angle. Melts with difficulty. Rotates a ray of polarized light to the right; $[\alpha]D = 31{\cdot}9°$.—On prolonged boiling with alcoholic potash it forms cholate of potash.—It is insoluble in water, but easily soluble in alcohol and in ether.

Cholate of Ethyl.

$$C^{52}H^{44}O^{10} = C^{4}H^{5}O,C^{48}H^{39}O^{9}.$$

HOPPE-SEYLER. *J. pr. Chem.* 89, 273.

Ethylic ether of cholalic acid.—Obtained by saturating alcoholic cholic acid with hydrochloric acid gas, allowing the liquid to stand for some time, precipitating with water, shaking the precipitate with ether and potash, and allowing the ether to evaporate. The crystalline mass thus formed is washed with water and recrystallised from alcohol or ether.

Delicate silky needles, exerting a right-handed action on polarized light; $[\alpha]D = 32{\cdot}4°$.—At a temperature of 100° to 120°, it is converted by alcoholic or aqueous ammonia into the ammonia salt of cholic acid, without yielding an amide.

Glycocholic Acid.

$$C^{52}NH^{43}O^{12} = C^{4}NH^{4}O^{3},C^{48}H^{39}O^{9}.$$

TIEDEMANN & L. GMELIN. *Die Verdauung.* Tübingen, 1824; 1, 43 and 51.

AD. STRECKER. *Ann. Pharm.* 65, 1; abstr. *Pharm. Centr.* 1848, 129; *J. pr. Chem.* 46, 137; *N. J. Pharm.* 13, 215; *Chem. Gaz.* 1848, 149.—*Ann. Pharm.* 67, 1; abstr. *Pharm. Centr.* 1848, 881 and 897; *J. pr. Chem.* 46, 143; *N. J. Pharm.* 15, 153; *Kopp's Jahresber.* 1847 *and* 1848, 896.—*Ann. Pharm.* 70, 149; abstr. *Pharm. Centr.* 1849, 660 and 673; *Chem. Gaz.* 1849, 427; *N. J. Pharm.* 16, 450; *Kopp's Jahresber.* 1849, 536.

Mulder. *Scheik. Onderz.* 5, 1; *Kopp's Jahresber.* 1847 and 1848. 896.
Hoppe-Seyler. *Arch. für pathol. Anatom.* 15, 126; *Chem. Centr.* 1859, 65. — *J. pr. Chem.* 89, 257; *Chem. Centr.* 1864, 129; *Anal. Zeitschr.* 2, 258; *Kopp's Jahresber.* 1863, 651.

Cholic acid of Gmelin and Strecker, different from the cholic acid of other chemists. — Discovered by Gmelin in 1824; investigated chiefly by Strecker.

Source As soda-salt (also as potash- and ammonia-salts) in the bile of most animals. Abundant in ox-bile (Strecker). See also *Handbuch*, viii. 40. Enderlin (*Ann. Pharm.* 75, 154) observed crystals of the acid in ox-bile which had become sour.

Preparation. 1. Fresh ox-bile is precipitated with neutral acetate of lead, and the yellow flocks are collected, washed with cold water, dissolved in alcohol, and decomposed with hydrosulphuric acid. The filtered liquid, warmed and mixed with a quantity of water sufficient to produce turbidity, and allowed to stand for 12 hours, deposits crystals, which are treated with boiling water, when a portion, chiefly paraglycocholic acid, remains undissolved, whilst the filtrate yields crystals of glycocholic acid on standing and very careful evaporation (Strecker).

According to Mulder, the glycocholic acid thus obtained contains ammonia: he therefore dissolves it in baryta-water, frees the solution from excess of baryta by means of carbonic acid, precipitates with acetic acid, and recrystallises. Delffs (*N. Jahrb. Pharm.* 6, 63) employs 1 part of neutral acetate of lead to 5 parts of purified dry bile: with a larger quantity of the acetate the precipitate cakes together, and is decomposed with difficulty by hydrosulphuric acid.

2. Ox-bile, evaporated over a water-bath and dried at 120°, is dissolved in the smallest possible quantity of absolute alcohol, and the solution is mixed with a little ether, whereby a deeply coloured syrupy or pasty precipitate is thrown down, from which the red solution is decanted and mixed with more ether. The liquid, which is thus rendered turbid, deposits, on standing, a large quantity of radiated needles, which must be washed with ether-alcohol containing $\frac{1}{10}$th of ether, and dried over oil of vitriol, since they deliquesce in the air. The crystals consist of glycocholate and taurocholate of soda, and contain small quantities of potash and ammonia. Their aqueous solution, mixed with a quantity of dilute sulphuric acid sufficient to produce turbidity and left to itself for some hours, deposits glycocholic acid, which is washed with cold water and recrystallised from boiling water (Strecker).

When fresh bile is precipitated with sulphuric acid, and the precipitate is washed with dilute sulphuric acid and covered with a layer of ether, a large quantity of crystals of glycocholic acid form in the precipitate (Strecker).

3. Bile is incompletely precipitated with neutral acetate of lead; the precipitate is dissolved in hot alcohol; the solution is decomposed with carbonate of soda; the filtrate is evaporated; and the residual glycocholate of soda is dissolved in absolute alcohol and precipitated with ether. An aqueous solution of the crystals, mixed with sufficient dilute sulphuric acid to produce turbidity, deposits glycocholic acid, which is to be washed and recrystallised (Hoppe-Seyler).

Properties. Very delicate white needles, which, when pressed between blotting paper, aggregate into laminæ, having a faint silky lustre, and an intensely sweet, somewhat acrid, bitter taste (Strecker). Reddens litmus strongly (L. Gmelin; Strecker). — Rotates a ray of polarised light to the right; in alcoholic solution $[\alpha]D = 29°$ (as determined for Fraunhofer's line D): the rotatory power is not affected by dilution, but is diminished by neutralising the solution with soda-ley (Hoppe-Seyler).

	Needles dried at 100°.		Strecker. *mean* (6).	Mulder. *mean* (3).	Rost van Tonningen.
52 C	312	67·10	67·05	66·70	66·45
N	14	3·01	3·23	3·25	
43 H	43	9·25	9·32	9·27	9·15
12 O	96	20·64	20·40	20·78	
$C^{52}NH^{43}O^{12}$	465	100·00	100·00	100·00	

According to Mulder $C^{54}NH^{44}O^{13}$.

Decompositions. 1. Glycocholic acid *heated* above 100° gives off water and melts to colourless glycocholonic acid (Strecker, *Handwörterb.* [2] 2, 2, 1192). — 2. It yields by *dry distillation* a large quantity of brown empyreumatic oil, and pale-yellow alkaline water. In the open fire it melts to a brown oil, emitting a smell of burnt horn, and afterwards an aromatic odour, and burns with a smoky flame. — 3. It dissolves easily and abundantly in fuming *nitric acid*, evolving a large quantity of gas: the yellow solution throws down, on addition of water, white flocks, a solution of which in aqueous ammonia is not precipitated by lime-water (Gmelin).

4. Glycochclic acid dissolves freely in *oil of vitriol* and in strong *hydrochloric acid*, forming solutions from which it is precipitated unaltered by water. The solutions become turbid on standing or when boiled, from separation of products which are formed from glycocholic acid by elimination of water, and are converted into glycocoll and choloïdic acid by continued boiling. The latter body is further transformed into dyslysin. The product first formed is glycocholonic acid (p. 62); after boiling a few minutes longer, the resin produced contains 72·6 p. c. C., and 9·1 H., corresponding to the formula $C^{52}NH^{39}O^{8}$, so that glycocholic acid loses 2 atoms of water twice in succession (Strecker).

Glycocholic acid, or its soda-salt, when heated with oil of vitriol, runs together into a colourless resin, which slowly dissolves with saffron-yellow colour, changing to red or brown-red on warming: the solution mixed with water deposits white, green, or brown flocks according to the temperature at which the solution was effected. If the resin produced by oil of vitriol be rinsed with water, without entirely removing the acid, and then heated till it becomes coloured, it absorbs oxygen and afterwards yields with alcohol a green solution, which when evaporated, with constant stirring, leaves a deep indigo-coloured residue (Frerichs & Städeler, *Müller's Arch.* 1856, 55; *Kopp's Jahresber.* 1256, 710). Neukomm (*Ann. Pharm.* 116, 30) and Enderlin (*Ann. Pharm.* 75, 174) made similar observations. This residue dissolves in alcohol, forming a gall-green solution. It is coloured yellow or orange by alkalis, green by hydrochloric acid, and deep-green, changing to greenish-blue or greenish-brown, red, and dirty-yellow, by nitric acid

(Städeler, *Ann. Pharm.* 132, 350). Cholic and taurocholic acids likewise behave in a similar manner.

5. Glycocholic acid breaks up, on boiling with *alkalis* or *baryta-water*, into glycocoll and cholic acid:

$$C^{52}NH^{43}O^{12} + 2HO = C^{4}NH^{5}O^{4} + C^{48}H^{40}O^{10}.$$

Small quantities of ammonia and a volatile oil are also formed as bye-products. — 6. On warming glycocholic acid with *sugar* and *oil of vitriol*, a fine purple-red colour is produced: Pettenkofer's *bile-test* (p. 66). — 7. Glycocholic acid undergoes decomposition much less readily than taurocholic acid in the *putrefaction* of bile (Strecker).

Combinations. Glycoholic acid dissolves in 303 parts of cold, and in 120 parts of boiling *water* (Strecker). — It dissolves easily in aqueous ammonia, alkalis, and baryta-water, forming salts. The solutions are precipitated by acids, including acetic acid (see taurocholic acid), the glycocholic acid being thrown down as a resin, which is converted into needles on standing, or more rapidly on addition of ether. A portion of the acid may be converted by this treatment into paraglycocholic acid (p. 57). — The salts are for the most part soluble in water, and have a very sweet taste (Gmelin): they dissolve in alcohol (Strecker).

Glycocholate of Ammonia. — The easily formed solution of glycocholic acid in aqueous ammonia leaves on evaporation a transparent gum, which reddens litmus slightly, evolves ammonia when treated with potash, and dissolves completely in water (L. Gmelin). When ammonia-gas is passed into a solution of glycocholic acid in absolute alcohol, crystals of the ammonia-salt, resembling those of the soda-salt, make their appearance on standing, or more rapidly on addition of ether. They give off ammonia in a vacuum or when boiled, and then have an acid reaction (Strecker).

Acid Salt? — *a.* According to Mulder, the ammoniacal glycocholic acid obtained by the first process (p. 57) is an acid salt which is not altered by recrystallisation. — *b.* When dry glycocholic acid is exposed to a current of gaseous ammonia, and afterwards to a current of air for a quarter of an hour, 100 parts of the acid retain 6·4 parts of ammonia: on continuing the current of air, a part of the ammonia is given off, and after the lapse of an hour there remain 1·6 parts of ammonia to 100 parts of acid (Mulder).

Dried over oil of vitriol, or at 130°.			Mulder. *a. mean.*
104 C	624	65·89	65·63
3 N	42	4·43	4·70
89 H	89	9·40	9·16
24 O	192	20·28	20·51
$2C^{52}NH^{43}O^{12},NH^{3}$	947	100·00	100·00

Strecker rightly regards this salt as a mixture (Kr.).

Glycocholate of Potash resembles the soda-salt (Strecker).

Glycocholate of Soda. — Occurs in bile. — Glycocholic acid is neutralized with aqueous carbonate of soda, or the alcoholic acid is shaken with the powdered carbonate: in either case the filtrate is evaporated, and the residue is dissolved in absolute alcohol and mixed with ether, whereupon radiated groups of white needles quickly appear (Strecker). The salt exerts a right-handed action on polarised light; [α]D in aqueous solution = 20·8°, in alcoholic solution = 25·7° (Hoppe-Seyler). — It melts when heated, and burns with smoky flame, leaving carbonate and cyanate of soda. — Dissolves very easily in water, and is precipitated by excess of soda-ley as an amorphous soft resin. Soluble in 27·2 parts of absolute alcohol at 15°, from which it is deposited in crystals by very slow evaporation, otherwise as an amorphous mass (Strecker). Ether throws down from the alcoholic solution an amorphous precipitate, in the absence of water; but if the solution be first mixed with sufficient ether to produce a strong turbidity, and then with water till the turbidity disappears, crystals quickly make their appearance (Städeler, *J. pr. Chem.* 72,257; *Kopp's Jahresber.* 1857, 562).

			Strecker.	Mulder.
			mean, at 100°.	*at* 130°.
52 C	312	64·06	63·11	64·1
N	14	2·87		
42 H	42	8·62	8·74	8·7
11 O	88	18·09		
NaO	31	6·36	6·14	6·3
$C^{52}NH^{42}NaO^{12}$	487	100·00		

According to Strecker, the salt dried at 100° is anhydrous, but according to Mulder it loses 2·47 p. c. of water between 110° and 130°.

Acid? — When carbonate of soda is added to glycocholic acid to slightly acid reaction, the solution evaporated, and the residue exhausted with absolute alcohol, there crystallises out, according to Mulder, an acid salt, which, after drying at 100°, loses 1·6 p. c. of water at 130° and then contains 4·5 p. c. of soda.

Glycocholate of Baryta. — Obtained by dissolving glycocholic acid in baryta-water, removing excess of baryta by means of carbonic acid, and evaporating. — Amorphous white mass, soluble in 6·24 parts of water at 15°, less freely in absolute alcohol, from which it does not crystallise (Strecker). — After drying at 100°, it loses 0·8 p. c. water at 120 — 130° (Mulder).

			Strecker.	
	at 100°.		*mean.*	Mulder.
52 C	312	58·60	58·27	58·6
N	14	2·63		
42 H	42	7·88	8·06	8·0
11 O	88	16·54		
BaO	76·4	14·35	14·35	14·1
$C^{52}NH^{42}BaO^{12}$	532·4	100·00		

The glycocholates do not precipitate salts of *strontia*, *lime*, or *magnesia* (Strecker).

Glycocholate of Lead. — Neutral acetate of lead produces no precipitate in cold aqueous glycocholic acid: the basic acetate occasions slight turbidity. The neutral acetate throws down flocks from the neutral salts, but a small portion still remains in solution and may be precipitated by the basic acetate (Gmelin; Strecker). — The salt is obtained by dissolving glycocholic acid in excess of carbonate of soda, precipitating with neutral acetate of lead, washing the precipitate and exhausting it with alcohol, whereby a solution is obtained from which water throws down the lead-salt (Mulder).

	at 130°.		Rost van Tonningen.
52 C	312	54·93	54·9
N	14	2·45	
42 H	42	7·39	7·5
11 O	88	15·49	
PbO	112	19·74	18·5 and 19·5
$C^{52}NH^{42}PbO^{12}$	568	100·00	

The aqueous acid is not precipitated by *stannous chloride*, *ferric chloride*, *sulphate of copper*, *mercurous nitrate*, or *nitrate of silver* (Gmelin). *Ferric chloride* throws down from the neutral salts yellowish flocks, soluble in alcohol. *Nitrate of silver* produces in solutions of neutral salts containing 1 p. c. of the acid, a dense gelatinous precipitate, partially or completely soluble on boiling, and becoming converted on slow cooling or on addition of ether, into needles which are slightly coloured by exposure to light (Strecker).

Glycocholic acid dissolves freely in *acetic acid*, very easily in *alcohol*, and very slightly in *ether*. The solutions yield crystals when very slowly evaporated. The alcoholic solution yields a resin, which cannot be completely reconverted into crystals. The alcoholic solution turns milky on addition of water, and deposits needles on standing for 24 hours. (Strecker). The acid dissolves, like cholic acid, in *glycerin* (Beneke).

Paraglycocholic Acid.

$C^{52}NH^{43}O^{12} = C^4NH^4O^3.C^{48}H^{39}O^9$.

AD. STRECKER. *Ann. Pharm.* 65, 12.

Paracholic Acid.—The precipitate thrown down by sulphuric acid from aqueous glycocholate of soda dissolves only partially on repeated boiling with water, pearly laminæ composed of microscopic six-sided tables remaining undissolved; similar laminæ together with needles of glycocholic acid, are also deposited from the decoctions. These laminæ are insoluble in boiling water, and are thereby distinguished from glycocholic acid, which they resemble in other properties and in composition, and into which they are transformed, either by precipitating their alcoholic solution with water or by dissolving them in alkalis (Strecker).

When glycocholate of baryta is decomposed by weak acetic acid, the glycocholic acid separated is completely soluble in boiling water, and is therefore free from paraglycocholic acid, whereas on decomposing the same salt with hydrochloric acid, a quantity of paraglycocholic acid is formed which is greater the stronger the hydrochloric acid employed (Mulder).

Laminæ at 100°.			Strecker. *mean.*	Mulder. *at* 130°.
52 C	312	67·10	67·30	66·7
N	14	3·01	2·73	3·5
43 H	43	9·25	9·28	9·2
12 O	96	20·64	20·69	20·6
$C^{52}NH^{43}O^{12}$	465	100·00	100·00	100·0

Glycocholonic Acid.

$$C^{52}NH^{41}O^{10} = C^{4}NH^{3}O^{2},C^{48}H^{38}O^{8}.$$

STRECKER. *Ann. Pharm.* 67, 20; 70, 166.
MULDER. *Scheik. Onderz.* 5, 51.

Cholonic acid.

The first product of the action of acids on glycocholic acid, afterwards breaking up into choloïdic acid and glycocoll (Strecker).

Preparation. 1. When a solution of glycocholic acid in strong hydrochloric or sulphuric acid is heated, there separate, on cooling, oily drops of glycocholonic acid, which afterwards solidify. The product is purified by dissolving it in aqueous ammonia, precipitating with chloride of barium, and decomposing the precipitate with dilute hydrochloric acid (Strecker).—2. Ox-gall freed from mucus is precipitated with neutral acetate of lead; the washed precipitate is suspended in water and decomposed by hydrosulphuric acid; the sulphide of lead is washed with cold water; and the acids thrown down with it are extracted by boiling water. The sulphide of lead remaining undissolved gives up to alcohol, glycocholonic acid, which is at once deposited in crystals, together with an amorphous mass, on addition of a little water. The crystals are separated from the amorphous sticky mass, dissolved in alcohol, and precipitated with water. The product still contains paraglycocholic acid and ammonia, from which it is freed by treating it with baryta-water, separating the insoluble glycocholonate of baryta from the soluble glycocholate, and decomposing with hydrochloric acid (Mulder). Since the lead precipitate of ox-gall contains chloride of lead, the subsequent treatment with hydrosulphuric acid sets free hydrochloric acid, which converts glycocholic into glycocholonic acid (Strecker).

Properties. Translucent, highly lustrous needles, or amorphous colourless resin. Has an acid reaction (Mulder).

at 120°—130°.			Strecker. Amorphous.	Mulder. Needles. *mean.*
52 C	312	69·82	70·54	69·45
N	14	3·13		3·30
41 H	41	9·15	9·46	9·42
10 O	80	17·90		17·83
$C^{52}NH^{41}O^{10}$	447	100·00		100·00

Mulder's formula is $C^{54}NH^{42}O^{11}$.

Glycocholonic acid breaks up, on boiling with *hydrochloric acid*, into glycocoll and choloïdic acid, the latter being transformed into dyslysin.

Glycocholonic acid is insoluble in water, either cold or boiling. Its solution in aqueous *ammonia* is precipitated by carbonate of ammonia, sal-ammoniac, and other salts. It dissolves in aqueous *alkalis* (Strecker).

Glycocholonate of soda.—Obtained by dissolving the acid in aqueous carbonate of soda, mixing the solution with alcohol, filtering from the precipitated carbonate of soda, and precipitating with ether. The precipitate may be crystallised by dissolving it in absolute alcohol and evaporating. After drying at 110° it does not lose water at 130°.— It dissolves in water more easily than glycocholate or paraglycocholate of soda (Mulder).

			Mulder. *mean.*
52 C	312	66·52	66·15
N	14	2·98	2·60
40 H	40	8·53	8 95
9 O	72	15 35	15 70
NaO	31	6·62	6·60
$C^{52}NH^{40}NaO^{10}$	469	100·00	100·00

The soda-salt precipitates *baryta-* and *lime-salts* in dense flocks (Strecker). The baryta-salt, which is insoluble in water, dissolves in a large quantity of alcohol (Mulder).

The acid is easily soluble in *alcohol*, nearly insoluble in *ether* (Mulder).

Taurocholic Acid.

$C^{52}NH^{45}S^2O^{14} = C^4NH^6S^2O^5,C^{48}H^{39}O^9.$

AD. STRECKER. *Ann. Pharm.* 65, 130; 67, 30; 70, 169.
HEINTZ (and LIEBERKÜHN). *Heintz's Lehrbuch der Zoochemie*, Berlin, 1853, 366.
F. HOPPE-SEYLER. *J. pr. Chem.* 89, 257 and 281.
PARKE. *Krit. Zeitschr.* 10, 55.

Choleic acid (Strecker).— Discovered by Strecker in 1848. In the form of soda-salt, and frequently accompanied by glycocholate of soda, it forms the principal constituent of the bile of most animals.

History of the investigation of Bile.—1. In 1806 Thénard (*Mem. de la Soc. d'Arcueil*, 1, 23; *N. Gehl.* 4, 511; *Traite*, Ed. 4, 4, 382) obtained from ox-gall a bile-resin, agreeing with choloïdic acid, together with *picromel*. The latter body is soluble in water, and, according to Thénard, is precipitated, according to Gmelin, not precipitated, by cold acids, and leaves carbonate of soda when burnt. Its properties seem to indicate that it is a mixture of taurocholate of soda with other bile-acids.

2. In 1814 Berzelius (*Schw.* 10, 488) obtained from bile a body which he termed *bile-substance* (*Gallenstoff*), and which he regarded as

a principal constituent of bile. This body was precipitated by excess of sulphuric acid from bile previously deprived of mucus, and was freed from sulphuric acid by treatment with carbonate of baryta (potash, lime), the bile-substance being then re-dissolved.

3. L. Gmelin's investigation of ox-gall, in 1826, led to the conclusion that bile contains 22 different substances, the most important of which are bile-resin, picromel, taurine, (glyco)cholate of soda, fats, and cholesterin.

4. Demarçay, in 1838, recognized the principal constituent of bile as a soda-salt. According to him, bile is not completely precipitated by neutral or basic acetate of lead, because aqueous acetate of soda (or lead) dissolves the lead-salt of the bile-acid, the dissolved portion not differing essentially from the precipitate. In his view, bile contains only one acid, Demarçay's *choleïc acid*, Liebig's *bile-acid*, which is said to be decomposed by hot acids into choloïdic acid and taurine and by alkalis into ammonia and cholic acid.

5. In 1840 Berzelius (*Ann. Pharm.* 33, 139; 43, 1; *Lehrbuch*, 4 Aufl. 9, 248) found, as the principal constituent of bile, a body called *bilin*, which, though neutral, was capable of combining with acids and bases, but could not be prepared in the pure state on account of its instability. By decomposition with acids it yielded taurine, then two resinous acids (*fellic* and *cholic* acids), and lastly dyslysin, and was capable of combining with these acids to form *bilifellic* and *bilicholic* acids, which were soluble in water.

6. Kemp (*J. pr. Chem.* 28, 154) supported the view of Demarçay, that bile is the soda-salt of a single acid, but found this acid to differ from Demarçay's choleic acid, and also from the bilin of Berzelius.

7. Theyer and Schlosser (*Ann. Pharm.* 48, 77; 50, 235) from analyses (1) of purified ox-gall, (2) of the precipitate formed by basic acetate of lead, and (3) of the soda-salt reproduced from the lead precipitate, also arrived at the conclusion that bile contains *one* acid in combination with soda. They showed further that the body remaining in solution after precipitation with basic acetate of lead, Berzelius's bilin, possesses the composition and properties of the soda-salt of bile-acid.

8. In all the foregoing investigations the presence of sulphur in bile-acid and in its decomposition-product, taurine, was overlooked. After Redtenbacher (ix, 285) had detected the presence of sulphur, and Platner (*Ann. Pharm.* 51, 105) had described a process for obtaining crystals of the soda-salt of bile-acid [which crystals were analysed by Verdeil (*Ann. Pharm.* 59, 311)], Strecker showed, in 1848, that ox-bile contains the soda-salts of two acids, glycocholic and taurocholic. Strecker's investigation, moreover, established the composition of the two acids, and their relation to the decomposition-products of bile, and completely refuted Berzelius's supposition as to the existence of an indifferent bilin.

9. Mulder, who previous to the publication of Strecker's investigation (*Scheik. Onderz.* 4. 1) had sought, by means of numerous analyses, to uphold Berzelius's views as to the nature of bile, as well as to con-

fute the supposition of the existence of a bile-acid, afterwards asserted (*Schiek. Onderz.* 5, 1) that Strecker's glycocholic acid was a decomposition-product of the bilin of fresh bile. He disputed the pre-existence of any crystallisable product in bile, the chief constituent being slimy, resinous, and unstable; and further endeavoured to prove the incorrectness of all Strecker's formulæ for the bile-acids. His views have met with no acceptation. See also Strecker's criticism (*Ann. Pharm.* 70, 154).

Taurocholic acid was not isolated by Strecker from ox-bile. Its composition was deduced from the decomposition-products of that portion of the bile which is soluble in alcohol and precipitable by ether, which products are cholic acid, glycocoll, and taurine. Its composition was arrived at also by analysing the salts of the bile-acids (mixed glycocholates and taurocholates), the proportion of taurocholic acid in which may be determined from the amount of sulphur they contain.

Source. Taurocholic acid occurs, together with varying proportions of glycocholic acid, in the bile of most animals, generally in combination with soda. It occurs free from glycocholic acid in dog's bile (Strecker), and in that of *Python tigris* (Schlossberger and Binder, *Ann. Pharm.* 102, 91), together with a little glycocholic acid in the bile of fishes, and of the sheep, wolf, fox, domestic fowl, goat (Strecker), shad-fish (Schlossberger and Vogtenberger, *Ann. Pharm.* 108, 66), and sturgeon (Scherer); together with a large proportion of glycocholic acid in the bile of the ox (Strecker), and kangaroo (Schlossberger, *Ann. Pharm.* 140, 244). See also *Handbuch* viii, 40.

Preparation. 1. Ox-bile is precipitated with neutral acetate of lead, not in excess; the precipitate is separated by filtration, and to the filtrate basic acetate of lead is added in small portions, the liquid being filtered after each addition, till the precipitate thrown down appears white and plaster-like. The taurocholic acid is then precipitated by excess of the basic acetate, with addition of ammonia, and the lead-salt is purified by repeatedly dissolving it in alcohol and precipitating with water, and afterwards decomposed by hydrosulphuric acid. The solution of free taurocholic acid thus obtained is decanted from the sulphide of lead and evaporated in a vacuum, the syrupy liquid first formed puffing up and ultimately becoming converted into a yellow tumefied mass (Heintz).

2. An alcoholic solution of decolorized dog's bile is evaporated; the residue is dissolved in a small quantity of alcohol, and mixed with ether, whereby taurocholate of soda is precipitated, an aqueous solution of which is precipitated with basic acetate of lead and a little ammonia. The precipitated lead-salt is suspended in boiling absolute alcohol, and decomposed with hydrosulphuric acid, and the filtered liquid is concentrated and mixed with a large excess of ether, taurocholic acid then separating in the form of a syrup, in which crystals form on standing (Parke).

Salts of taurocholic acid are also obtained from fish-bile. See below.

Properties. Delicate silky needles (Parke). White amorphous powder (Heintz). In the form of soda-salt it exerts a right-handed action on polarised light (Hoppe-Seyler).

Decomposition. 1. Dry taurocholic acid is decomposed only at temperatures considerably above 100° (Parke). According to Heintz, it is not completely soluble in water after being heated to 100°; the aqueous and alcoholic solutions also undergo decomposition, and turn milky when evaporated with the aid of heat (Strecker. Heintz). — 2. Taurocholic acid breaks up into cholic acid and taurine when boiled for four hours with *baryta-water:*

$$C^{52}NH^{45}S^{2}O^{14} + 2HO = C^{4}NH^{7}S^{2}O^{6} + C^{48}H^{40}O^{10} \text{ (Strecker).}$$

The same decomposition is effected by heating the acid to 100° with water in a sealed tube (Parke).

This property of taurocholic acid was established by experiments with an acid containing glycocholic acid, and not with the isolated acid. When purified bile is precipitated with neutral acetate of lead, and the precipitate containing glycocholate of lead is removed, basic acetate of lead throws down from the filtrate a mixture of basic glycocholate and taurocholate of lead, containing varying quantities of oxide of lead, carbon, and hydrogen. When the precipitate is decomposed by boiling baryta-water, the filtrate boiled with excess of baryta-water for twenty-four hours, and the residue freed from excess of baryta by means of carbonic acid, a filtrate is obtained, from which hydrochloric acid throws down cholic acid. This filtrate freed from baryta by sulphuric acid, from sulphuric and hydrochloric acids by hydrated oxide of lead, and from lead by hydrosulphuric acid, leaves on evaporation taurine, together with glycocoll, arising from the decomposition of glycocholic acid (Strecker).

3. A solution of the taurocholate of an alkali, mixed with excess of *acid,* becomes turbid on boiling, from separation of choloidic acid, the solution then containing taurine (Strecker). — 4. *Ozone* does not act upon aqueous taurocholates of the alkalis, but oxidizes them completely after addition of excess of alkali, forming carbonic and sulphuric acids, but neither taurine nor bile-acid. Taurocholates of the alkalis, mixed with glycocholates, behave in a similar manner (v. Gorup-Besanez, *Ann. Pharm.* 110, 86; 125, 218).

5. Taurocholic acid, heated with *oil of vitriol* behaves like glycocholic acid (p. 58); when mixed with *oil of vitriol* and *sugar,* it assumes a violet-red colour (Pettenkofer's *bile-test*). Ox-bile, mixed with not too much sugar, and then with oil of vitriol till the precipitate formed at first is dissolved, yields a deep violet liquid resembling the aqueous solution of permanganate of potash. This coloration is obtained also with decolorized bile (Pettenkofer, *Ann. Pharm.* 52, 90).

In testing for bile, the liquid to be examined is mixed with two-thirds of its volume of oil of vitriol, in such a manner that the temperature does not rise above 60°, and the mixture is shaken with 2 to 5 drops of a solution of cane-sugar, whereupon the violet colour appears, provided that the temperature has not been allowed to rise too high, and that neither albumin, nor a large quantity of metallic chlorides, nor too much sugar is present. Hydrochloric acid acts in a similar manner to oil of vitriol, but the colour produced is less intense (Pettenkofer). — The principal constituents of bile yield this coloration, which, however, is produced without the addition of sugar, on mixing bile with oil of vitriol, and dropping water into the mixture (van der Broek, *J. pr. Chem.* 39, 363). When inspissated bile is triturated with oil of vitriol, and water is dropped into the mixture, there is produced, even without addition of sugar, a violet-red coloration, changing to dark-blue in 15 or 20 minutes (Vogel, jun., *N. Jahrb. Pharm.* 3, 150). See also xv, 322, and Neukomm (*Ann.*

Pharm. 116, 30). According to Huppert (*Zeitschr. anal. Chem.* vi, 294) the presence of oxidizing substances (nitrates and chlorates) interferes with this reaction.

The *salts* of taurocholic acid, in as pure a state as possible (but not quite free from glycocholic acid), exhibit the following characters. Those of the alkalis are neutral, very sweet, with a bitter after-taste, hygroscopic, but not deliquescent, and permanent in the air. They dissolve in water, forming a frothing liquid, and in alcohol. Ether converts them, on prolonged contact, into radiated crystalline masses. Their aqueous and alcoholic solutions are not decomposed by evaporation. The aqueous solution is not precipitated by acetic acid, hydrochloric acid, or oil of vitriol, nor the alcoholic by carbonic acid. Moreover the presence of these salts in glycocholates of the alkalis (as obtained from ox-bile, for example) prevents the precipitation of glycocholic acid by acetic acid, or a small quantity of a mineral acid, whilst, on the other hand, the resinous precipitate produced by a large quantity of sulphuric acid in a mixture of glycocholates and taurocholates of the alkalis invariably contains taurocholic acid. — The taurocholates of the alkalis are thrown down from their aqueous solutions by strong potash-ley and by carbonate of potash, but not by chlorides of the alkali-metals, or by sulphates. — Taurocholates of the alkalis dissolve fats, fatty acids, and cholesterin (Strecker).

Taurocholate of Potash. — From fish-bile. That of *Gadus Morrhua* and *Pleuronectes maximus*, contains chiefly potash; that of *Esox lucius* and *Perca fluviatilis* more soda.

The strongly dried bile is dissolved in absolute alcohol, and the filtrate is mixed with a little ether, which precipitates colouring matter, together with a small quantity of the other constituents, after the removal of which the precipitation is completed by the addition of more ether. The salt thus thrown down contains (besides potash) ammonia, magnesia, and soda, to remove which its concentrated aqueous solution is precipitated with cold strong potash-ley. The precipitated flocks are washed with potash-ley, and freed from excess of potash by dissolving them in absolute alcohol, passing carbonic acid through the solution, and filtering from the deposited carbonate. The taurocholate of potash then remaining in solution may be obtained either by evaporation or by precipitation with ether. — Colourless needles resembling wavellite (Strecker).

	Dried at 120°.		Strecker.
52 C	312	56·41	56·8
N	14	2·53	
44 H	44	7·94	8·1
13 O	104	18·80	
2 S	32	5·78	
KO	47·1	8·54	8·8
$C^{52}NH^{44}KS^{2}O^{14}$	553·1	100·00	

Taurocholate of Soda. — From dog-bile. Precipitated by ether from an alcoholic solution of the inspissated bile, in amorphous, slightly coloured flocks, which are transformed under ether into crystalline needles (Strecker. Hoppe-Seyler).

Schlieper (*Ann. Pharm.* 60, 109) dissolved the inspissated bile of *Boa annaconda* in absolute alcohol, decolorised the solution, washed the residue with ether, re-dissolved in absolute alcohol, and evaporated the solution, whereby he obtained a yellow, friable, very hygroscopic gum, which, according to Strecker, is taurocholate of soda. — Exerts a dextro-rotatory action on polarised light: $[\alpha]D$ for the soda-salt dissolved in water = 21·5°, for the salt dissolved in alcohol = 24·5° (Hoppe-Seyler).

Dried at 120° to 130°.			Schlieper.	Strecker.
52 C	312	58·10	58·13	58·2
N	14	2·60	3·41	
44 H	44	8·19	8·51	8·2
13 O	104	19·36	18·69	
2 S	32	5·98	6·23	5·9
NaO	31	5·77	5·03	5·8
$C^{52}NH^{44}NaS^2O^{14}$	537	100·00	100·00	

The substances formerly described as *purified bile*, *crystallised bile*, *soda-salt of bile-acid*, are mixtures of taurocholate and glycocholate of soda, containing also potash and ammonia. Platner (*Ann. Pharm* 51, 105; 59, 311), gave directions for the preparation of these crystals, agreeing in part with those above given (p. 57). Verdeil (*Ann. Pharm.* 59, 311) analysed the crystals obtained from ox-bile. Bensch (*Ann. Pharm.* 65, 194), analysed the purified bile of the calf, sheep, bear, fowl, fish, and goat; Strecker that of various fishes. All these mixtures contain 52 atoms of carbon and 43 to 44 atoms of hydrogen to 1 atom of base (Strecker).

Taurocholate of Baryta. — Obtained by neutralizing the acid with hydrate of baryta, evaporating over the water-bath, dissolving the residue in absolute alcohol, and mixing it with a small quantity of ether, whereupon the salt is thrown down as a resin, afterwards becoming crystalline (Lieberkühn).

The taurocholates of the alkalis do not precipitate salts of *baryta*, *lime*, or *magnesia*, even after addition of ammonia (Strecker).

Taurocholate of Lead. — Neutral acetate of lead does not precipitate taurocholate of soda: the basic acetate produces white flocks, which dissolve in a large excess of the precipitant and also on boiling, reappearing as the liquid cools. — After filtering from the lead precipitate, ammonia throws down a further quantity, but even then a large quantity of taurocholate remains in solution (Strecker).

The precipitates thrown down by basic acetate of lead from purified ox-bile, and analysed by Theyer and Schlosser, Verdeil, Strecker, and Mulder, were mixtures of taurocholate and glycocholate of lead (Strecker).

Taurocholates of the alkalis precipitate from *acetate of copper*, after addition of ammonia, bluish-white flocks, which dissolve in a larger quantity of ammonia (Strecker). The copper-salt dissolves in water less easily than in alcohol, and is therefore precipitable from aqueous, not from alcoholic solutions (Lieberkühn). — Taurocholates of the alkalis give with alcoholic *ferric chloride* a precipitate which disappears on further addition of the iron-salt. *Stannous chloride* and *mercurous nitrate* throw down white flocks. *Mercuric chloride* produces no precipitate. *Nitrate of silver* does not precipitate the solutions, even after addition of ammonia, but reduces them on boiling (Strecker).

Taurocholic acid dissolves easily in *alcohol*, slightly in *ether* (Strecker).

Biliary Acid from Guano.

F. Hoppe-Seyler. *Virchow's Archiv.* 26, 525; *Chem. Centr.* 1863, 755; *Kopp's Jahresber.* 1863, 654.

Occurs in Peruvian guano. The same or a similar acid occurs in pigeon's dung.

An extract of guano, made with cold water, is evaporated, till the oxalate of ammonia crystallises, and afterwards precipitated with hydrochloric acid. After standing for some time, the precipitate is collected, washed, and dissolved in alcohol, and the solution, after being decolorised, is evaporated, with addition of carbonate of soda. The residue is exhausted with absolute alcohol, and the extract is freed from alcohol, dissolved in water, and precipitated with chloride of barium. From this precipitate the acid is separated by hydrochloric acid.

The acid does not crystallise. It has an acid reaction, and does not rotate a ray of polarised light. It is free from sulphur, and when pure probably free from nitrogen. — When *heated* it burns with aromatic odour. With *oil of vitriol* and *sugar* it gives the violet-red colour of the bile-acids. Oil of vitriol dissolves it, forming a green fluorescent solution. It is decomposed by boiling with *hydrochloric acid*, yielding a product resembling dyslysin.

The acid is insoluble in *water*, but easily soluble in aqueous *ammonia* and *alkalis*. — The baryta-salt dissolves in hot water, and is deposited in the form of a resin on evaporating the solution. It contains 70·9 p.c. C., 8·2 H., 0·5 N., and 12·7 Ba, or 44 atoms of hydrogen to 32 atoms of carbon. — The acid dissolves in *alcohol*, from which it is precipitated by water and by ether.

Appendix to Bile-acids.

Bile-pigments.

Thénard. *Traité de Chimie.* ed. 4, 4, 580.
Chevreul. *Majendie J. de Physiol.* 4, 259. — *Ann. de Mus.* 1825, 378.
L. Gmelin. *Tiedemann u. Gmelin, Die Verdauung,* 1, 79.
Bolle. *Br. Arch.* 38, 266.
Berzelius. *Lehrbuch,* 3 Aufl. 9, 281. — *Ann. Pharm.* 43, 53.
Platner. *Ann. Pharm.* 51, 110.
Scherer. *Ann. Pharm.* 53, 383.
Bramson. *Zeitschr. für rationelle Medicin,* 4, 193.
Schmid (u. Wackenroder). *N. Br. Arch.* 41, 291 and 294.
Hein. *J. pr. Chem.* 40, 47; *Kopp's Jahresber.* 1847 and 1848, 920.
Heintz. *Pogg.* 84, 106; *Kopp's Jahresber.* 1851, 605.
Brücke. *J. pr. Chem.* 77. 22; *Chem. Centr.* 1859, 248; *Kopp's Jahresber.* 1859, 637.
Maly. *Wien. Akad. Ber.* 49, 498; *Krit. Zeitschr.* 7, 656; *Ann. Pharm.* 132, 127; *Chem. Centr.* 1865, 75; *Kopp's Jahresber.* 1864, 663; further *J. pr. Chem.* 104, 28; *Jahresb.* 1868, 824.

STÄDELER. *Ann. Pharm.* 132, 323; *Par. Soc. Bull.* 1864, 57; *Kopp's Jahresber.* 1864, 657. — Further: *Epistolary Communication.*
THUDICHUM. Tenth report of the Medical Officer of the Privy Council, p. 240; *J. pr. Chem.* 104, 193; abstr. *Krit. Zeitschr.* 11, 555; *Chem. Centr.* 1868, 609; *Bull. Soc. Chim.* [2] 10, 498; *Jahresb.* 1868, 826.
JAFFE. *J. pr. Chem.* 104, 401; *Zeitschr. f. Chem.* [2], 5, 666.

In the bile of the higher classes of animals, more abundantly in certain gall-stones, also in jaundiced urine, and in the serum of blood and chyle, there exist colouring matters, which, when their solutions are mixed with nitric acid [nitrous acid according to Millon (*Compt. rend.* 14, 904)] exhibit a change of colour from green to blue, violet, red, and finally yellow: Gmelin's *Pigment reaction.*

Calculi consisting of bile-pigments are brown, crumbly, and ochry, and evolve an animal odour when burnt. They are only slightly soluble in water and alcohol, but dissolve in potash with dark-brown colour. Nitric acid produces the pigment-reaction. — When burnt they leave a large quantity of ash, which contains carbonate of lime, the lime occurring in the concretion partly as carbonate (Bolle; Scherer) and partly as a compound of lime and colouring matter (Heintz), which is insoluble in alcohol (Bramson). — After exhaustion with water, alcohol, and ether, the pigment gall-stones contain 74 p. c. C., 6·3 H., and 14·4 N., besides ammonia and carbonic acid in the mineral substance. When the latter are removed by means of hydrochloric acid, the residual pigment contains 62·49 p. c. C., 8·17 N., 6 15 H., and 23·18 O. (Scherer), but it is still a mixture, containing, besides pigment, epithelium and other bodies (Heintz).

The pigment of ox gall-stones is Gmelin's *bile-brown*, which passes into *bile-green* when exposed to the air in alkaline solution (Gmelin). The yellow pigment of human gall-stones forms the *cholepyrrhin* of Berzelius, who obtained from inspissated ox-gall a pigment which differed from cholepyrrhin, and to which he gave the name *bilifulvin* when in combination with bases (lime, soda) and *bilifulvic acid* in its isolated condition.

Virchow (*Ann. Pharm.* 78, 352) found crystals of bilifulvin in unhealthy bile and liver, and compared them with hæmatoïdin, from which, however, they were found to differ. Valentiner (*Günzburg's Zeitschr.*, *J. pr. Chem.*, 77, 22) subsequently found that chloroform extracts bile from gall-stones; from jaundiced liver and many other tissues, crystals which give the pigment reaction with nitric acid. These crystals were regarded by Valentiner as identical with hæmatoïdin. Städeler (*Ann. Pharm.* 116, 29), however, showed that hæmatoïdin behaves differently with nitric acid, and possesses a different crystalline form. Jaffé, on the other hand, affirms the identity of bilifulvin with hæmatoïdin, on the ground of the following experiment.

An apoplectic clot containing a large quantity of crystals of hæmatoïdin, was dried, comminuted, moistened with absolute alcohol, and exhausted with chloroform, which, when evaporated in the dark, left golden-yellow crystals of hæmatoïdin. These crystals, after washing with ether, which partially dissolved them, dissolved in aqueous carbonate of soda, with yellow colour, turning green in the air, and gave the pigment-reaction with nitric acid (Jaffé, *Archiv. Pathol. Anat. und Physiol.* 23, 192; *Anal. Zeitschr.* 1, 259). — See also *Handbuch*, viii, 64.

Städeler obtained from human gall-stones, by Valentiner & Brücke's process, four pigments, one of which, the bilirubin, forming the principal part of the concretions, agreed with the biliphæin of Brücke, and the cholepyrrhin of Maly. Heintz's biliphæin has a different composition, but appears to resemble bilirubin in its decompositions and solubility.

1. Bilirubin.

Cholophæin, Cholepyrrhin.

Occurs abundantly in human gall-stones (Städeler), and ox-gall-stones (Thudichum). In human bile (Valentiner, Brücke). In small quantity in the bile of the ox and sheep (Maly).

Powdered human gall-stones are freed from cholesterin and fat by means of ether, and from bile by exhaustion with hot water. The residue is dried and boiled repeatedly with chloroform, which dissolves a small quantity only of colouring matter, and leaves it on evaporation as a greenish-brown sticky mass, together with microscopic yellow laminæ of bile-red. After exhaustion with chloroform, the residue is digested with dilute hydrochloric acid, which eliminates carbonic acid, and extracts lime, magnesia, and phosphoric acid, the principal part of the pigment remaining, however, undissolved, and appearing, after washing and drying, of a dark brownish-green colour. This residue is exhausted with boiling chloroform, which dissolves bilifuscin and bilirubin, and is afterwards freed from biliprasin by repeated treatment with alcohol, and from bilirubin by again boiling it with chloroform. Under this treatment, bilihumin still remains undissolved. — The chloroform solutions are evaporated; the residue is freed from bilifuscin by treating it with alcohol; the remaining bilirubin is dissolved two or three times in chloroform and evaporated; the residue is washed with ether and alcohol, and again dissolved in chloroform; and the solution, evaporated till it begins to deposit bilirubin, is precipitated with alcohol (Städeler). Thudichum proceeds essentially in the same manner as Städeler. Heintz exhausts the gall-stones with water, alcohol, ether, and hydrochloric acid in succession, dissolves the washed residue in hot aqueous carbonate of soda, precipitates the filtrate with hydrochloric acid without exposure to air, and washes the precipitated flocks with hot water.

Brücke agitates human bile with chloroform; separates, filters, and distils the yellow solution; and washes the residue first with 94 p. c. alcohol, which acquires a deep-brown colour, and afterwards with ether.

Thudichum exhausts pulverised and sifted ox-gallstones successively by decantation with hot water, boiling with alcohol, cold dilute hydrochloric acid, and again with alcohol; then further with ether, and after drying the powder, which then exhibits a fine reddish-yellow colour, boils it with chloroform, which, after repeated treatment, dissolves a part of the colouring matter, the rest only after repeated exhaustion of the residue with hydrochloric acid. The residue left after distilling off the chloroform, is washed with chloroform, and purified by solution in chloroform and precipitation with absolute alcohol. — Or the powder, exhausted first with chloroform, and then with hydrochloric acid, may be treated with alcoholic potash, the filtrate precipitated with hydrochloric acid, whereupon green colouring matter remains dissolved, and the precipitate purified by washing with warm absolute alcohol, or by agitation with chloroform. Part of the bilirubin then remains dissolved, and another portion may be precipitated from the concentrated chloroform solution by absolute alcohol (Thudichum).

Properties. Amorphous, orange-coloured, or crystalline dark-red powder, appearing in well formed crystals only when impure. The crystals obtained by agitating human bile with chloroform, according to Valentin's process, have convex faces, and differ greatly in their angles from the crystals of hæmatoïdin (Städeler). Thudichum obtained bilirubin in two modifications, namely, as a dark, red-brown crystalline powder: Thudichum's *cholophæin;* or of a pure red colour, in which case it consists either of amorphous grains, or when precipitated by alcohol of yellow rhombic prisms: Thudichum's *bilirubin.* The crystals reflect light with purple and steel-blue lustre. Dry red bilirubin becomes brown on exposure to light (Thudichum). Bilirubin dried over oil of vitriol, loses about 1 p. c., at 100°, and no more at 130° (Strecker).

Calculation according to Städeler.			Stadeler. *at* 120°—130°. *mean.*	Maly. *at* 100°.
32 C	192	67 13	67·13	67·16
2 N.	28	9·79	9·59	
18 H	18	6·29	6·19	6·20
6 O	48	16·79	17·09	
$C^{32}N^{2}H^{18}O^{6}$	286	100·00	100·00	

Calculation according to Thudichum.			Thudichum. *at* 120°—130°. *mean.*
18 C	108	66·26	66·01
N	14	8 59	9·03
9 H	9	5·52	6·01
4 O	32	19·63	18·95
$C^{18}NH^{9}O^{4}$	163	100·00	100·00

Städeler's substance contained traces of sulphur. Maly's analysis agrees closely with Städeler's formula, and not at all with Thudichum's.

The dark olive-brown biliphæin of Heintz contains at 130°, 60·87 p. c. C., 9·12 N., and 6·05 H., corresponding with the formula $C^{32}N^{2}H^{18}O^{9}$. See also Hein's analyses of impure cholepyrrhin, containing ash (*J. pr. Chem.* 40, 47).

Decompositions. 1. Bilirubin *heated* in a glass tube melts, puffs up, and evolves yellow vapours having a disagreeable odour (Städeler). Hein's biliphæin decomposes without melting.

2. Bilirubin dissolves in cold, strong nitric acid, forming a deep-red solution, which turns cherry-red on warming or standing, and remains of that colour for several days. Nitric acid containing 20 p. c. of the monohydrate, produces, on warming only, dark-violet resinous flocks, which turn pale-brown and dissolve with yellow colour on boiling. Alkaline solutions of bilirubin, mixed with an equal volume of alcohol, are coloured by strong commercial nitric acid, yellow, green, blue, violet, ruby-red, and dirty-yellow in succession, even when very dilute. Bilirubin dissolved in chloroform is coloured dark-violet and ruby-red on dropping nitric acid into the solution. Each of these colours may be rendered permanent by mixing the solution with a large quantity of alcohol. On dropping red fuming nitric acid into ammoniacal bilirubin, and afterwards nearly neutralising the liquid with ammonia, green flocks are pro-

duced, which gradually turn blue, and, after washing with water, give up green colouring matter to alcohol, the blue remaining behind in the form of a dark powder (Städeler).

The tints produced by the action of nitric acid containing nitrous acid on bile-pigments, correspond to characteristic alterations of the spectrum. The solution of the blue modification exhibits in the spectrum a broad absorption-band between the Fraunhofer lines, C and D, resolved, on dilution, into two narrower bands (α and β), which are separated by a bright band situated near D. Between b and F there is another absorption-band, γ. As the action of the nitric acid goes on, the bands α and β gradually disappear, while γ becomes plainer, till at length, when the solution contains the red modification, γ likewise disappears.

To isolate the *blue pigment*, an alcoholic solution of biliverdin, or an ammoniacal solution of bilirubin containing alcohol, is mixed with strong fuming nitric acid till the liquid turns blue, and exhibits the two absorption-bands, α and β; the solution is then mixed with chloroform —ammonia being added from time to time to neutralize the acid—and shaken up with water, whereupon the chloroform takes up the colouring matter; the water is removed; the chloroform layer filtered from the biliverdin is evaporated to dryness; and the residue is purified by repeated solution in chloroform. The substance thus obtained has a dark violet colour, is insoluble in water, but dissolves easily, and with dark violet colour in alcohol, ether, and chloroform. Alkalis dissolve this pigment with brown violet colour; acids with fine blue colour. The neutral and alkaline solutions exhibit no absorption-bands, but the slightest trace of any acid brings out the bands α, β, and γ.—Cold strong sulphuric acid dissolves this pigment, forming a dark-green solution, from which water throws down green flocks soluble in alcohol, with green colour, and exhibiting with nitric acid the peculiar pigment reaction and the accompanying spectral phenomena. The liquid filtered from these flocks is blue by reflected, violet by transmitted light; is coloured brown by carbonate of soda; not decolorised by grape-sugar; and, therefore, does not exhibit the characters of indigo.

The pigment corresponding to the absorption-band γ, is obtained exactly as above, excepting that the action of the nitric acid must be continued till the bands α and β, vanish altogether. The substance thereby obtained is brown-red, and dissolves with fine ruby colour in alcohol, ether, and chloroform. The colour is not altered by the addition of alkalis or acids. The acid solution alone exhibits the band γ (Jaffé).

From human bile, dog's bile, or the alcoholic extract of either, dilute hydrochloric acid extracts a colouring matter, the red or reddish-yellow solution of which exhibits a band coinciding in position with γ, but darker and more sharply defined. By agitation with chloroform and evaporation, this pigment is obtained as a red residue, which is soluble in water, alcohol and chloroform, may be precipitated from its aqueous solution by chloride of calcium and by neutral or basic acetate of lead, and dissolved out of the precipitate by dilute hydrochloric acid. Soda-ley colours the hydrochloric acid solution light-yellow, and after a few minutes developes a new band near δ, between b and F, the band γ disappearing at the same time. The solution of the acid pigment in chloroform likewise exhibits the absorption band γ, but removed a few degrees nearer to b (Jaffé). Different from this is a blue bile-pigment, which is sometimes obtained from filtered bile by extraction with chloroform, treating the chloroform solution with dilute aqueous carbonate of soda, and neutralizing with hydrochloric acid (Ritter, *Deutsche chem. Gesellsch.* 3, 209).

3. Bilirubin dissolves in *oil of vitriol* to a brown liquid, which gradually turns violet-green, and from which water precipitates nearly black flocks, soluble in alcohol, with fine violet colour. — 4. Hot fuming *hydrochloric acid* produces dark-brown substances, which do not dissolve in ammonia after prolonged boiling in the acid. — 5. A small quantity of *chlorine-water* colours bilirubin dissolved in chloroform a fine green; a larger quantity of chlorine bleaches it. A similar effect is often produced, in the absence of chlorine-water, by commercial chloroform in a state of decomposition, which produces a green colouring matter, soluble in chloroform with green colour, but insoluble in ether. — 6. *Sodium-amalgam* reduces the colour of aqueous alkaline bilirubin to pale-yellow, but does not completely decolorise it, even when heated (Städeler).

7. Bilirubin dissolved in *alkalis* changes colour on exposure to the air, from absorption of oxygen. When boiled, even without access of air, the solution acquires a dark greenish-brown colour, and on addition of hydrochloric acid, deposits dark-green flocks, from which alcohol takes up biliverdin, leaving behind a dirty-yellow portion (Städeler). This transformation occurs also with the impure bile-pigments; in the case of Heintz's biliphæin, it is expressed by the equation, $C^{32}N^2H^{18}O^9 + O = C^{32}N^2H^{18}O^{10}$ (biliverdin according to Heintz). It is more probable that both water and oxygen are taken up, thus:—

$$\underset{\text{Bilirubin}}{C^{32}N^2H^{18}O^6} + 2HO + 2O = \underset{\text{Biliverdin}}{C^{32}N^2H^{20}O^{10}};$$

whilst, without access of air, a second product is formed, thus:—

$$2C^{32}N^2H^{18}O^6 + 4HO = C^{32}N^2H^{20}O^6 + C^{32}N^2H^{20}O^{10} \text{ (Städeler).}$$

Maly, from his earlier experiments, inferred that the conversion of chlolepyrrhin (bilirubin) into biliverdin was the result, not of absorption of oxygen, but of elimination of ammonia, and accordingly regarded biliverdin as an acid, and bilirubin as the corresponding amide. He now, however, abandons this view, and confirms the statement of Städeler, that the formation of biliverdin from bilirubin takes place by absorption of oxygen, and without elimination of ammonia. This conversion may be effected by *bromine* or *iodine*, by *acids* with access of air, by *alkalis* with access of air; more quickly on addition of *peroxide of lead* (Maly), or by *potassio-cupric tartrute* (Thudichum). Thudichum supposes that carbonic acid is given off, but has not actually observed it: $C^{18}NH^9O^4 + O^4 = C^{16}NH^9O^4 + 2CO^2$. Städeler gives the formula $C^{32}N^2H^{18}O^6 + O^2 = C^{32}N^2H^{18}O^8$.

a. In contact with *bromine-vapour* and moist air, bilirubin quickly turns green. When a dilute alcoholic solution of bromine is dropped into a solution of bilirubin or chloroform, the colour changes, according to the quantity of bromine, to green, dark blue which remains unaltered for weeks, then dirty-violet, dark wine-red, and ultimately light wine-red—the same changes of colour, therefore, as those produced by nitric acid containing nitrous acid (Maly).

b. When a solution of bilirubin in a mixture of chloroform and glacial acetic acid is heated in the water-bath in a half-filled sealed tube, formation of biliverdin takes place, provided the quantity of oxygen enclosed is sufficient; the same transformation is effected by hydrochloric, but not by sulphurous acid (Maly).

c. An alkaline solution of bilirubin kept from the air over mercury, remains red-brown for months; but on admitting oxygen into the tube, the liquid absorbs it, and turns green. This change from red-brown to green is more rapidly effected by peroxide of lead, or by platinum in contact with air, whereas permanganic acid gives rise to further oxidation (Maly).

Bilirubin is insoluble in *water* (Städeler).—It dissolves in aqueous *ammonia*, forming a deep orange-red solution, from which it is precipitated unaltered in orange flocks by hydrochloric acid, even after boiling. The yellow colour of the ammoniacal solution is perceptible in a two-inch layer of a solution containing only one-millionth part of bilirubin. Solutions containing $\frac{1}{40,000}$th of the substance colour the skin distinctly yellow.—Ammoniacal solutions turn paler and brownish-yellow in diffused light, and more rapidly in direct sunshine, and are afterwards not precipitated by hydrochloric acid (Städeler). See also Thudichum.

Bilirubin dissolves easily in aqueous caustic soda and its carbonate, with dark orange colour; excess of caustic soda precipitates brown flocks of the soda-compound. Bilirubin is withdrawn from its solution in chloroform by agitation with alkaline water (Städeler).

According to Thudichum, bilirubin forms basic, neutral, and half-acid salts, viz.: a. *Basic*, when an ammoniacal solution of bilirubin is precipitated by a lead or silver salt in excess. b. *Neutral*, by precipitation of the same solution with baryta or lime salts. c. *Half-acid*, when the ammoniacal solution of bilirubin is neutralized with excess of bilirubin previous to precipitation. Thudichum gives the following formulæ:

Baryta-salt, *a*. .	$C^{36}N^{2}H^{20}Ba^{2}O^{12} = 2C^{18}NH^{8}BaO^{4} + 4aq.$
Lime-salt, *a*	$C^{36}N^{2}H^{20}Ca^{2}O^{12} = 2C^{18}NH^{8}CaO^{4} + 4aq.$
Baryta-salt, *b* . .	$C^{54}N^{3}H^{29}Ba^{2}O^{16} = 2C^{18}NH^{8}BaO^{4} + C^{18}NH^{9}O^{4} + 4aq.$
Lime-salt, *b* ..	$C^{54}N^{3}H^{29}Ca^{2}O^{16} = 2C^{18}NH^{8}CaO^{4} + C^{18}NH^{9}O^{4} + 4aq.$
Zinc-salt.	$C^{54}N^{3}H^{29}Zn^{2}O^{16} = 2C^{18}NH^{8}ZnO^{4} + C^{18}NH^{9}O^{4} + 4aq.$
Lead-salt	$C^{18}NH^{7}Pb^{2}O^{4}.$
Silver-salt, *a* ...	$C^{18}NH^{7}Ag^{2}O^{4}.$
Silver-salt, *b*	$C^{18}NH^{8}AgO^{4} + 2aq.$

According to Städeler, bilirubin with the formula $C^{32}N^{2}H^{18}O^{6}$ contains as many as 3, or with the double formula $C^{64}N^{4}H^{36}O^{12}$, as many as 6 atoms of hydrogen replaceable by metals: accordingly Thudichum's salts may be represented by the following formulæ:

Lead-salt	$C^{64}N^{4}H^{30}Pb^{6}O^{12}.$
Silver-salt, *a*	$C^{64}N^{4}H^{30}Ag^{6}O^{12}.$
Baryta-salt, *a*....................	$C^{64}N^{4}H^{33}Ba^{3}O^{12}.$
Lime-salt, *a*	$C^{64}N^{4}H^{33}Ca^{3}O^{12}.$
Silver-salt, *b*	$C^{64}N^{4}H^{33}Ag^{3}O^{12}.$
Baryta-salt, *b*.........	$C^{64}N^{4}H^{34}Ba^{2}O^{12}.$
Lime-salt, *b*	$C^{64}N^{4}H^{34}Ca^{2}O^{12}.$
Zinc-salt	$C^{64}N^{4}H^{34}Zn^{2}O^{12}.$

Bilirubate of Ammonia. Dry bilirubin is not altered by dry ammonia gas, but forms with strong aqueous ammonia a dark-red mass, which dissolves in strong alcohol, but not in ether, gives off most of its ammonia on drying, and leaves bilirubin as a green-brown shining mass (Thudichum).

Bilirubate of Baryta. *a.* From ammoniacal bilirubin, chloride of barium throws down a greenish-brown precipitate which dries up at 100° to a dark-brown powder. Contains 44·58 p. c. C., 3·98 H., 27·56 Ba., and is therefore $C^{36}N^{2}H^{20}Ba^{2}O^{12}$ (calc. 43·46 p. c. C., 4·02 H., 27·56 Ba.) Thudichum. Städeler's formula requires 26·53 p. c. Ba.

b. Obtained as a brown-red precipitate in the same manner as *a*, but from a solution not containing excess of ammonia. Contains at 100° 51·50 p. c. C., 4·65 H., 20·63 Ba. Calc. for $C^{54}N^{3}H^{29}Ba^{2}O^{16} = C^{36}N^{2}H^{20}Ba^{2}O^{12} + C^{18}NH^{9}O^{4}$ = 49·09 p. c. C., 4·39 H., 20·75 Ba. (Thudichum); for $C^{64}N^{4}H^{34}Ba^{2}O^{12}$ = 19·38 Ba. (Städeler).

Bilirubate of Lime. *a.* Red precipitate thrown down by chloride of calcium from an ammoniacal solution of bilirubin. Contains at 100°, according to Thudichum, 52·35 to 54·96 p. c. C., 4·65 to 5·04 H., 9·63 to 11·02 Ca. (calc. for $C^{36}N^{2}H^{20}Ca^{2}O^{12}$ = 54·0 p. c. C., 5·0 H. and 10·0 Ca.)—According to Städeler it contains 9·10 p. c. Ca., and is represented by the formula $C^{64}N^{4}H^{33}CaO^{12}$; calc. 9·54 Ca.

b. The precipitate obtained from neutral solutions contains 60·37 p. c. C., 5·74 H., 6·79 to 7·03 Ca., and is therefore $C^{54}N^{3}H^{29}Ca^{2}O^{16}$ (calc. 57·54 C., 5·15 H., 7·1 Ca.) Thudichum. Städeler's formula, $C^{64}N^{4}H^{34}Ca^{2}O^{12}$ requires 6·56 p. c. Ca.

Bilirubate of Zinc. Reddish-brown precipitate, containing at 100° 11·3 to 12·03 p c zinc; perfectly insoluble in water. According to Thudichum, $C^{54}N^{3}H^{29}Zn^{2}O^{16}$ (calc. = 11·5 Zn.); according to Städeler, $C^{64}N^{4}H^{34}Zn^{2}O^{12}$ (calc. = 10·24 Zn.).

Bilirubate of Lead. The precipitate formed by excess of neutral lead acetate contains, when dried at 100°, 58·15 p. c. lead (calc. for $C^{18}NH^{7}Pb^{2}O^{4}$ = 56·25 Pb.), Thudichum. According to Städeler, $C^{64}N^{4}H^{30}Pb^{6}O^{12}$ with 52·32 p. c. Pb.

Bilirubate of Silver. *a. With a comparatively large quantity of silver.* When the clear mixture of ammoniacal bilirubin and excess of silver nitrate is neutralized with nitric acid, the resulting precipitate contains 55·86 to 56·81 p. c. Ag.—*b. With a comparatively small quantity of silver.* Reddish-brown precipitate thrown down by nitrate of silver from ammoniacal bilirubin made as neutral as possible. Contains on the average 37·39 p. c. Ag. (Thudichum).

a is, according to Thudichum, $C^{18}NH^{7}Ag^{2}O^{4}$ (calc. = 57·29 p. c. Ag.). *b* = $C^{18}NH^{8}AgO^{4}$ + 2aq. (calc. = 37·50Ag.). Städeler gives the formulæ $C^{64}N^{4}H^{30}Ag^{6}O^{12}$ (calc. = 53·38 p. c. Ag.), and $C^{64}N^{4}H^{33}Ag^{3}O^{12}$ (calc. = 36·28 Ag.).

Bilirubin dissolves in traces only in boiling *glacial acetic acid* and in *ether*. It is slightly soluble in hot but nearly insoluble in cold *alcohol*.—Amorphous bilirubin dissolves easily in cold *chloroform*, with yellow to pale orange-red colour: the crystalline substance dissolves on boiling. If the chloroform contains acid decomposition-products, as is frequently the case with that met with in commerce, the solution is of a fine green colour (Strecker). According to Thudichum, it dissolves in 586 parts of chloroform, forming a dark-red solution which turns brown and black on exposure to sunshine.—Bilirubin dissolves in *sulphide of carbon* and *benzol*, and in hot *oil of turpentine* and *oil of almonds* (Strecker). According to Maly it dissolves very slightly in *benzol* and *petroleum*, somewhat more freely in hot *fusel-oil*, *fat oils*, and *glycerin*, not in *albumin* or *saliva*.

2. Biliverdin.

Cholechlorin.

Occurs in human bile, but not in human gall-stones (Städeler).

According to Berzelius it is identical with leaf-green (xvii, 3), and like that substance can be obtained in three modifications. Barruel (*Ann. Scienc. natur.*, 19, 384) likewise finds the colouring matter of bile to resemble leaf-green very closely, and according to Filhol (*J. Chim. méd.* 1862; *Pharm. Viertelj*, 12, 557) this colouring matter, as well as that of the yolk of egg, may, like leaf-green, be resolved into blue and yellow. But biliverdin exhibits neither the fluorescence nor the absorption bands of leaf-green, from which it is thus sufficiently distinguished by its optical properties (Stokes, *Phil. Mag.* 28, 63; *Chem. Centr.* 1865, 64).

Formation. From bilirubin by oxidation. See p. 74.

When a solution of bilirubin in excess of soda-ley is exposed to the air in shallow dishes till it turns green, or when the red alkaline solution is boiled till it appears of a greenish-brown colour, hydrochloric acid throws down therefrom a splendid green precipitate of biliverdin, which is purified by dissolving it in alcohol (Städeler). Heintz treats crude bile-brown in a similar manner. The biliphæin remaining unaltered may be extracted by chloroform (Brücke). Thudichum prepares biliverdin either by passing air into a hot alkaline solution of bilirubin, or by boiling bilirubin with potassio-cupric tartrate, whereby a precipitate of cuprous oxide containing biliverdin is obtained. — Maly mixes a solution of bilirubin in chloroform with glacial acetic acid, and heats it in the water-bath in half-filled sealed tubes. Or he mixes alkaline bilirubin with peroxide of lead; precipitates biliverdin-lead by supersaturation with acetic acid; decomposes the precipitate with alcohol containing sulphuric acid; and precipitates the filtrate with water.

Nearly black substance, yielding a dark-green powder. Inodorous and tasteless (Heintz).

According to Städeler.			Heintz.
32 C	192	60·00	60·04
2 N	28	8·75	8·53
20 H	20	6·25	5·84
10 O	80	25·00	25·59
$C^{32}N^2H^{20}O^{10}$	320	100·00	100·00

According to Thudichum.			Thudichum. *mean.*	Maly. *at* 100°.
16 C	96	63·57	62·43	63·75
N	14	9·27	9·34	8·75
9 H	9	5·96	6·13	6·01
4 O	32	21·20	22·10	21·49
$C^{16}NH^9O^4$	151	100·00	100·00	100·00

Maly doubles the formula.

Hein, who examined biliverdin containing 7·88 p. c. of ash, found 65·65 p. c. C., and 6·62 H. — Heintz proposed the formula $C^{16}NH^9O^5$. Respecting the establishment of the above formula, see p. 76.

A concentrated alcoholic solution of biliverdin transmits only the green of the spectrum; a somewhat more dilute solution transmits also the yellow, orange, and part of the red, afterwards the blue and violet; very dilute solutions absorb the extreme red (Maly).

Biliverdin melts when *heated* and leaves on decomposition a large quantity of charcoal (Heintz). *Nitric acid containing nitrous acid* colours it blue, violet, red, and ultimately dirty yellow (Heintz). On boiling it with nitric acid, nitrous gas is evolved, and water added to the resulting solution throws down a yellow nitro-compound crystallisable from alcohol, while a fixed acid remains, yielding a crystalline silver-salt. — *Peroxide of lead* boiled with alcoholic biliverdin produces a brown substance; it colours ammoniacal biliverdin brown-red (Thudichum).

Reducing agents, such as *sulphuretted hydrogen*, *zinc* in acid solution, *sodium amalgam* in alkaline solution, alter biliverdin to a certain extent, but do not reconvert it into bilirubin. *Iodine* converts biliverdin into a black resin. *Chlorine* decomposes it immediately, forming yellowish flocks or resins containing chlorine, and partly soluble in chloroform (Thudichum).

When an alcoholic solution of biliverdin is treated with silver oxide, a purple substance, *bilipurpin*, is formed, but remains combined with the excess of silver oxide; ammonia dissolves this compound, and hydrochloric acid added to the solution sets the bilipurpin free. A delicate test for bile-pigments is obtained by boiling the substance under examination with an ammoniacal solution of silver oxide, filtering, and acidulating with hydrochloric acid, whereupon, if bile-pigments are present, a purple colour will be produced. By the prolonged action of silver oxide, bilipurpin is converted into a yellow substance, *biliflavin*. Mercuric oxide does not act sensibly on biliverdin; peroxides act upon it in the same manner as silver oxide (Thudichum).

Biliverdin is insoluble in cold *water*, and colours boiling water only faintly green (Heintz). It dissolves in boiling *hydrochloric acid* with dirty brownish-green colour (Berzelius; Hein). It dissolves in aqueous caustic *alkalis* and their *carbonates*, forming green solutions, from which it is precipitated by acids (Heintz); the alkaline solutions gradually turn brown, from formation of biliprasin (Städeler).

Chloride of barium throws down green flocks from the ammoniacal solution (Heintz). The *lime-compound* is likewise insoluble in water. The *lead-salt* is completely thrown down from alcoholic biliverdin in the form of a green precipitate (Maly).

According to Thudichum, biliverdin is not thrown down from its ammoniacal solution by chloride of barium or calcium; but from the alcoholic solution, baryta-water and lime-water throw down black-green precipitates, so likewise do the acetates of lead, mercury, and copper. The barium and calcium precipitates are soluble in water; the rest may be washed with water without decomposition. The *barium salt* gave by analysis 49·20 and 49·39 p. c. C., 4·34 and 4·43 H., 22·15 and 22·67 Ba, whence Thudichum deduces the formula:— $C^{48}N^{3}H^{27}Ba^{2}O^{14}$ or $2BaO,3C^{16}NH^{9}O^{4}$ (calc. 47·52 C., 4·45 H., 22·60 Ba). — The *calcium salt* gave by analysis (in mean numbers) 62·19 p. c. C., 5·74 H., and 5·64 Ca, whence Thudichum deduces the formula, $C^{144}N^{9}H^{77}Ca^{4}O^{36}$.

Biliverdin dissolves in *oil of vitriol*, and is precipitated by water (Maly). It dissolves easily in *alcohol*, forming fine dark-green solutions precipitable by water (Städeler), becoming grass-green on addition of the smallest quantity of acid (Maly). Insoluble in *ether* and in *chloroform* (Städeler). Dissolves easily in *methyl alcohol*, but is insoluble in *sulphide of carbon* and in *benzol*, very slightly soluble in *amyl alcohol* and *iodide of ethyl*, soluble in the latter and in chloroform in presence of alcohol. Soluble in *glacial acetic acid* (Maly).

3. Bilifuscin.

Obtained by evaporating its alcoholic solution (p. 71) and washing the residue with ether, which, however, dissolves bilifuscin as well as fatty acids. The product is freed from adhering bilirubin by washing with chloroform, then dissolved in alcohol and evaporated. — Nearly black, shining, brittle mass, triturable to a dark olive-brown powder. — When heated, or when treated with nitric acid, it behaves like bilirubin. It is insoluble in water, but dissolves easily in aqueous ammonia or soda, with dark-brown colour, which is not changed to green by hydrochloric acid. The solution in soda-ley decomposes in the air. The ammoniacal solution is precipitated in dark-brown flocks by chloride of calcium. — Bilifuscin is easily soluble in alcohol, with deep-brown colour; nearly insoluble in ether and chloroform (Städeler).

	at 120°.		**Städeler.**
32 C	192	63·16	63·07
2 N	28	9·21	
20 H	20	6·58	6·59
8 O	64	21·05	
$C^{32}N^2H^{20}O^8$	304	100·00	

Contains 2 atoms HO more than bilirubin (Städeler).

4. Biliprasin.

This body is contained in the alcoholic solution (p. 71), together with a little bilirubin, from which it is freed by evaporation and treatment with ether and chloroform. The residue is dissolved in a little cold alcohol and evaporated. — Shining, nearly black crusts, triturable to a greenish-black powder. — When heated it melts and puffs up. With nitric acid it behaves like bilirubin, but the blue coloration is indistinct. — It is insoluble in water, but dissolves in aqueous caustic alkalis, and less freely in carbonates, with brown colour. When these solutions are exposed to the air, bilihumin is formed. Acids precipitate the alkaline solutions or, in presence of alcohol, colour them green. — Bilihumin dissolves easily in alcohol, with pure green colour. The solution is brown in presence of ammonia only. — It is insoluble in ether and in chloroform (Städeler).

	Dried at 100°.		Städeler.
32 C	192	56·81	56·81
2 N	28	8·28	7·42
22 H	22	6·51	6·52
12 O	96	28·40	29·25
$C^{32}N^2H^{22}O^{12}$	338	100·00	100·00

After deducting 0·6 p. c. of ash.

5. Bilihumin.

This substance remains undissolved when gall-stones are treated successively with ether, water, aqueous acids, chloroform, alcohol, and weak ammonia, but is still contaminated with mucus, epithelium, and other bodies. It is digested, in the moist state, in moderately strong aqueous ammonia, at 50° to 60°, so long as that liquid takes up anything of importance; the filtrate is precipitated with hydrochloric acid, and the precipitate is washed and boiled repeatedly with alcohol. The product still contains ash-constituents. — Black powder, with a tinge of olive after drying. It dissolves very slowly in aqueous ammonia and in warm dilute soda-ley, forming a deep brown solution which is coloured like that of biliverdin by addition of alcohol and nitric acid containing nitrous acid, the red colour being especially distinct (Städeler).

Green pigment from the Gall-stone of an Ox. — Extracted from the triturated gall-stone, after exhaustion with water, alcohol, and ether, by carbonate of soda, and precipitated from the brown alkaline solution by hydrochloric acid. The green flocks thus obtained were freed from a yellow impurity insoluble in alcohol, by dissolving them in ether, evaporating to perfect dryness, and taking up the residue with alcohol. — Dark-green powder, containing, to 32 at. C., 2·5 at. N., 18·5 H., and 10 O., and consequently richer in nitrogen than the pigment of human bile. Gives the pigment-reaction with nitric acid. Dissolves in aqueous alkalis with brown colour, in alcohol with green colour, and sparingly in ether (Städeler, *Ann. Pharm.* 132, 349).

The pigment of Serpent's bile (from *Python amethystinus*) resembles biliverdin. Berzelius exhausted the inspissated bile with cold alcohol, boiled the residue with ammoniacal alcohol, and evaporated the solution, whereupon the colouring matter remained as a greenish-black, hard, tasteless mass, free from ammonia. It gives the pigment-reaction with nitric acid, and dissolves in potash-ley, forming a dark-green solution, from which acids precipitate green flocks. It is soluble also in acetic acid, the solution being coloured yellow by water; in cold, and more freely in hot alcohol, but not in ether (Berzelius, *Pogg.* 18, 88).

Bizio (*Brugn. Giorn.* 15, 453; *Schw.* 37, 110) obtained from an unhealthy bile, green crystals having peculiar properties, to which he gave the name *erythrogen*. — See the third German edition of this Handbook, 2, 1160.

The *pigment of Pig's bile* is precipitated, together with mucus and hyoglycocholic acid, by acetic acid. The precipitate is lemon-yellow and dissolves in alcohol, forming a solution of a golden-yellow colour, which on exposure to the air, gradually changes to dark-green, and ultimately to blood-red. These colours are produced more rapidly by warming the solution with a little hydrochloric acid. The red colour dissolves in ether (Strecker).

Green pigment from Jaundiced Urine. — This urine, which is of a yellow to brown colour when fresh, becomes darker, and often green, on standing. — The urine, freed from mucus and uric acid by filtration, is precipitated with chloride of barium. The pale-green precipitate is collected, washed, and decomposed (*a*) by boiling with aqueous soda. The yellow solution thus obtained is precipitated with hydrochloric acid; the precipitate is separated by filtration, and dissolved in ether-alcohol; and the solution is slowly evaporated, the pigment being then left as a friable dark-green mass, which is to be freed from hydrochloric acid by washing with water. Or (*b*) the baryta precipitate is decomposed with hydrochloric acid and alcohol, the filtrate evaporated, the residue washed with water and dissolved in ether-alcohol, the solution evaporated, and the residue again washed with water. — Fine dark-green powder. — When submitted to prolonged digestion with hydrochloric acid, or when gently warmed with alkalis for some time, it gradually turns blackish-brown. In both cases it loses the property of giving the pigment-reaction with nitric acid, and becomes more soluble in water and less soluble in alcohol. After digestion with hydrochloric acid for fourteen days it has the composition *c*, and after treatment with warm alkalis for fourteen days the composition *d*. — The pigment is nearly insoluble in water, but dissolves easily in aqueous alkalis with yellowish-brown colour, in aqueous and absolute alcohol, and sparingly in ether (Scherer, *Ann. Pharm.* 53, 377).

Analyses by Scherer.

	a.	*b.*	*c.*	*d.*
C	67·59	68·19	61·84	62·09
N	6·70	7·08	9·08	7·10
H	7·64	7·47	6·46	6·56
O	18·07	17·26	22·62	24·25
	100·00	100·00	100·00	100·00

Heintz (*Pogg.* 84, 106) and Städeler (*Ann. Pharm.* 132, 349) consider the pigment impure, the latter chemist regarding it as a decomposition-product formed by the action of hydrochloric acid. — On a similar colouring matter from jaundiced urine, see Braconnot (*J. Chim. méd.* 3, 480).

Primary Nucleus $C^{48}H^{48}$.

Cerosin.

? $C^{48}H^{48}O^2 = C^{48}H^{48},O^2$.

AVEQUIN. *Ann. Chim. Phys.* 75, 218; *J. Pharm.* 26, 738; *J. Chim. méd.* 17, 73; *J. pr. Chem.* 22, 238; *Ann. Pharm.* 37, 170.
DUMAS. *Ann. Chim. Phys.* 75, 222; *Ann. Pharm.* 37, 222.
LEWY. *N. Ann. Chim. Phys.* 13, 451.

Wax of the Sugar-cane. Cerosie.

On the bark of the sugar-cane, especially the violet variety, there occurs a white dust, which is easily scraped off with a knife; a portion of it is also separated when the cane is crushed, and then floats on the surface of the juice. It is purified from leaf-green and colouring-matter by washing with cold alcohol, and afterwards dissolved in hot alcohol. On evaporating the solution, cerosin remains behind (Avequin). Dumas obtains it in crystals by cooling the alcoholic solution.

The wax from New Granada, *Cire des Andaquies*, after being treated with boiling water, melts at 77°, is of sp. gr. 0·917 at 0°, and contains 81·06 p. c. C., 13·55 H., and 4·79 O. It is composed of 50 p. c. of palm-wax, 45 p. c. of cerosin, and 5 p. c. of a substance allied to cerolein. On boiling it with 15 or 16 parts of alcohol, the cerosin is dissolved and separates in the form of a jelly on cooling (Lewy).

Delicate, pearly laminæ, which do not produce a greasy stain on paper (Dumas). Yellowish, very hard, of smooth fracture, and triturable to a white powder. Sp. gr. 0·961 at 16°. Melts at 82° and solidifies at 80°, crystallising in needles during the partial solidification of large quantities. Permanent in the air (Avequin; Lewy).

According to Lewy.			Dumas.	Lewy. *a.*	Lewy. *b.*
48 C	288	81·82	81·4	81·56	81·56
48 H	48	13·62	14·1	13·66	13·73
2 O	16	4·56	4·5	4·78	4·71
$C^{48}H^{48}O^{2}$	352	100·00	100·0	100·00	100·00

b. From *Cire des Andaquies* (Lewy). Dumas proposed the earlier formula $C^{48}H^{50}O^{2}$, and regarded cerosin as an alcohol allied to ethal.

Cerosin burns from a wick with a white flame (Avequin). — It forms with *oil of vitriol* a conjugated acid, the baryta-salt of which is easily soluble (Lewy). — It combines with *alkalis*, but not readily (Dumas). — Cerosin, heated to 250° with *potash-lime*, evolves hydrogen and yields cerosic acid (Lewy).

Cerosin is insoluble in cold alcohol of 36°, but perfectly soluble in the boiling liquid, from which it does not crystallise on cooling: 1 part of the wax in 144 parts of alcohol forms a jelly when cold. — It is insoluble in cold, and slightly soluble in hot *ether*, crystallising in small granules on cooling (Avequin).

Cerosic Acid. — Obtained by heating cerosin to 250° with potash-lime. The product is boiled with water containing hydrochloric acid, and the cerosic acid thereby set free is washed repeatedly with boiling water and converted into baryta-salt, which is freed from any cerosin remaining undecomposed by exhausting it with boiling alcohol. The baryta-salt is decomposed with boiling hydrochloric acid, and the cerosic acid thus obtained is dissolved in rectified rock-oil, and recovered from the filtrate by evaporation. — White crystalline substance, melting at 93·5°. — Dissolves with difficulty in boiling alcohol and ether. Contains 80·13 p. c. C., 13·39 H., and 6·38 O., corresponding to the formula $C^{48}H^{48}O^{3}$ (Lewy). Probably $C^{68}H^{68}O^{4}$? (Kr.) (calc. 80·31 p. c. C., 13·38 H.).

Gingkoic Acid.

$$C^{48}H^{48}O^{4} = C^{48}H^{48},O^{4}.$$

SCHWARZENBACH. *Verhandl. der phys. med. Gesellsch. in Würzburg*, 1857, 276; *Pharm. Viertelj.* 6, 424; abstr. *N. Jahrb. Pharm.* 19, 77.

Occurs in the sarcocarp of *Gingko biloba*. Concerning this plant see Hanbury (*N. Jahrb. Pharm.* 19, 77). — According to Wittstein, Peschier's gingkoic acid must be regarded as impure acetic acid.

The ethereal extract of the fruit leaves on evaporation a yellow acid oil which solidifies to a crystalline mass on cooling. The crystals are coloured brown, and cannot be decolorised by animal charcoal, and only partially by treating the lead-salt with hydrosulphuric acid. They have an acid reaction, melt at 35° and solidify at 10°. They form a soap with potash-ley; a baryta-salt sparingly soluble in water, but easily soluble in alcohol; a yellow sticky lead-salt; and a silver-salt containing 22·72 p. c. of silver (calc. for $C^{48}H^{47}AgO^4$ requires 22·74 p. c. Ag.), insoluble in alcohol and very slightly soluble in ether.

	Acid.		Schwarzenbach.
48 C	288	78·26	78·33
48 H	48	13·04	13·33
4 O	32	8·70	8·34
$C^{48}H^{48}O^4$	368	100·00	100·00

APPENDIX TO COMPOUNDS CONTAINING 48 ATOMS OF CARBON.

1. Laserpitin.

$$C^{48}H^{36}O^{14} = C^{28}H^{22}O^8,2C^{10}H^7O^3.$$

A. FELDMANN. *Ueber das Laserpitin, Dissertation.* Göttingen, 1865; *Krit. Zeitschr.* 8, 292.

In the white gentian-root of *Laserpitium latifolium.*

The finely comminuted dry root is exhausted with 80 p. c. alcohol at 60°; the tincture is freed from alcohol by distillation; and the residue is set aside until the upper layer becomes granular and crystalline. It is then pressed and washed with weak alcohol, and afterwards purified by the following treatment. Its alcoholic solution is precipitated with alcoholic neutral acetate of lead and filtered; the filtrate is treated with hydrosulphuric acid; and the sulphide of lead thereby formed is boiled with alcohol, which leaves on evaporation colourless crystals of laserpitin. These crystals lose a little adhering acetic acid by exposure to the air.

Properties. Colourless rhombic prisms, inodorous and tasteless alone, but very bitter in alcoholic solution. Neutral. Slightly heavier than water. Melts at 114°, without loss of weight, forming a colourless oil, which solidifies to an amorphous resin and afterwards becomes crystalline. When more strongly heated it volatilises and condenses in oily drops. Free from nitrogen.

			Feldmann.
48 C	288	66·05	66·03
36 H	36	8·26	8·38
14 O	112	25·69	25·59
$C^{48}H^{36}O^{14}$	436	100·00	100·00

Decompositions. Alcoholic laserpitin turns brown when heated with strong *potash-ley*, and breaks up into laserol and angelic acid.

$$C^{48}H^{36}O^{14} + 2HO = C^{28}H^{22}O^{8} + 2C^{10}H^{8}O^{4}.$$

If the solution be heated till the whole of the alcohol is expelled and then mixed with an excess of dilute sulphuric acid, brown resinous flocks are deposited, of which a further quantity is obtained on distilling off the angelic acid. These flocks dissolve in alcohol with red-brown colour, and are deposited from the solution on evaporation in yellow amorphous grains, which afterwards become crystalline and cannot be decolorised by animal charcoal. They taste acrid and peppery, dissolve in alcohol and ether, and form with potash-ley a yellow solution, from which acids throw down an amorphous precipitate. This body is Feldmann's *laserol*. After drying over oil of vitriol it contains 65.85 p. c. C., and 8.76 H., corresponding to the formula $C^{28}H^{22}O^{8}$ (calc. 66.14 p. c. C., 8.66 H.).

Laserpitin heated with *caustic potash* evolves an odour of mint. — It is not affected by dry *hydrochloric acid gas*. When heated to 150° with fuming hydrochloric acid, it is partially dissolved, with cherry-red colour, the residue melting to a brown resin. Dilute sulphuric likewise effects no splitting up of the body, even at 250°. — Its cherry-red solution in *oil of vitriol* and the solution in fuming *nitric acid* yield white precipitates on addition of water.

Laserpitin is insoluble in cold and boiling *water*, in dilute and strong *acids*, including glacial acetic acid, and in aqueous *ammonia*, *potash* and *soda*.

It dissolves in 12.34 parts of *bisulphide of carbon*, easily in *chloroform*, in 9 parts of absolute *alcohol*, in 21.73 parts of 85 p. c. alcohol, and in 3.6 parts of *ether*. When rapidly evaporated, these solutions leave amorphous laserpitin, which melts more easily than the crystallised substance, and is more readily dissolved. The alcoholic solution is rendered milky by water, and deposits microscopic crystals, which combine in curdy masses when shaken. The alcoholic solution is not precipitated by iodide of potassium, neutral acetate of lead, corrosive sublimate, or nitrate of silver.

Laserpitin dissolves easily in *benzene*, *oil of turpentine*, and *fat oils*.

2. Coniferin.

$$C^{48}H^{32}O^{24}.$$

W. Kubel. *J. pr. Chem.* 97, 243.

Discovered by Th. Hartig; investigated by Kubel. — Occurs in the cambium of pine and fir trees, more especially the following: *Abies excelsa* and *A. pectinata*, *Pinus Strobus*, *P. Cembra*, *Larix europea.*

Preparation. From the cambium obtained from trees felled and peeled at the time of the formation of new wood. The cambium is scraped off the surface of the wood, and the scrapings are pressed.

The sap is heated to boiling, and filtered to separate coagulated albumin and other substances; the filtrate is evaporated down to $\frac{1}{5}$th; and the crystals which form after cooling are purified by recrystallisation from boiling water and weak spirit, with the help of animal charcoal. The crystals are dehydrated by drying at 100°. — Melts at 185° and solidifies in a glassy mass.

	Dried at 100°.		Kubel. *mean* (5).
48 C	288	56·25	55·80
32 H	32	6·25	6·38
24 O	192	37·50	37·82
$C^{48}H^{32}O^{24}$	512	100·00	100·00

Coniferin when *heated* turns brown and carbonises, evolving an aromatic odour. — It dissolves in *oil of vitriol*, forming a dark-violet solution, from which water throws down a blue precipitate. — The solution in cold strong *hydrochloric acid* deposits a blue precipitate when warmed. — Coniferin is decomposed by boiling with dilute *mineral acids*, with emission of a vanilla-like odour, and separation of a blue resinous substance; at the same time dextrose is produced. The resin dissolves in soda-ley with yellow colour, and is precipitated from the solution by acids.

Combinations. With Water. Crystallised Coniferin. — Very delicate, white, silky, pointed needles or warts, which effloresce in dry air and give off all their water of crystallisation at 100°. — Tastes slightly bitter. — Rotates a ray of polarised light to the left.

	Crystals.		Kubel. *mean.*
$C^{48}H^{32}O^{24}$	512	90·46	
6 HO	54	9·54	9·49
$C^{48}H^{32}O^{24} + 6aq$	566	100·00	

Coniferin dissolves in 196 parts of cold water, and very freely in boiling water. The solution is not precipitated or coloured by *caustic soda*, *neutral* or *basic acetate of lead*, or *sesquichloride of iron*.

It is slightly soluble in strong *alcohol*, insoluble in *ether*.

COMPOUNDS CONTAINING 50 ATOMS OF CARBON.

Primary Nucleus $C^{50}H^{40}$; *Oxyazo-nucleus* $C^{50}NH^{37}O^{2}$.

Solanidine.

$$C^{50}NH^{39}O^{2} = C^{50}NH^{37}O^{2},H^{2}.$$

Zwenger & Kind. *Ann. Pharm.* 118, 129.
O. Gmelin. *Ann. Pharm.* 110, 167.
A. Kromayer. *N. Br. Arch.* 116, 114.

Formed, together with dextroglucose, by heating solanine with dilute mineral acids.

A solution of solanine in very dilute sulphuric acid is boiled till it turns yellow and begins to show signs of turbidity. It is then left to cool, and the crystalline precipitate of sulphate of solanidine is washed with a little water and decomposed by digesting its alcoholic solution with carbonate of baryta. The resulting precipitate contains sulphate and carbonate of baryta, and solanidine, the last of which is extracted from the washed and dried mixture by boiling absolute alcohol. The alcoholic solution, when cooled and concentrated, deposits the solanidine, first in white, afterwards in yellowish crystals, which are separated from any undecomposed solanine by dissolving them in ether, and purified by recrystallisation from ether (Zwenger & Kind). — Or, solanine is decomposed by boiling with dilute hydrochloric acid; the hydrochlorate of solanidine which separates is purified by dissolving it in alcohol and precipitating with ether; an alcoholic solution of the purified salt is decomposed with ammonia, and the precipitate is crystallised from alcohol and ether (Zwenger & Kind).

When dilute acids are employed for the extraction of solanine, the crude product leaves a crystalline residue of hydrochlorate of solanidine, on treating it with hydrochloric acid (O. Gmelin).

Properties. Long, colourless, very delicate silky needles, or, as occasionally obtained from ether, shorter four-sided prisms. It does not undergo alteration at 100°, but melts at 200° [a little above 200° (Kromayer)] to a yellowish mass, which solidifies in radiated crystals. At a higher temperature it sublimes, leaving very little charcoal. Its alcoholic solution is bitter and acrid, but the solid substance is nearly tasteless. — It is more strongly alkaline than solanine.

	Dried in a vacuum.		O. Gmelin.	Zwenger & Kind. *mean.*
50 C	300	81·30	82·00	80·92
N	14	3 77		3·79
39 H	39	10·59	10·71	11·15
2 O	16	4 34		4·14
$C^{50}NH^{39}O^{2}$	369	100·00		100·00

O. Gmelin's solanidine turned yellow at 100°, and was therefore impure. On the formula of solanidine, see *Solanicine* and *Solanine*.

Decompositions. 1. Solanidine slowly *heated* to 200° acquires a yellow or reddish colour. — 2. Cold strong *nitric acid* converts it into a red oil; the hot acid dissolves and oxidises it with violence. — 3. *Oil of vitriol* colours solanidine red, and afterwards dissolves it to a dark-red liquid, with formation of sulphate of solanicine and modified solanidine (p. 88), which substances are precipitated by water, or when formed with oil of vitriol containing water, are slowly deposited as a yellow precipitate. — 4. Solanidine is not affected by boiling strong *potash-ley*, or by *cuprate of potash*, *nitrate of silver*, or *chloride of gold* (Zwenger & Kind). — 5. On dropping *iodine-water* into alcoholic solanidine, the solution is first decolorised and afterwards deposits yellowish-brown flocks (Kromayer).

Solanidine is very slightly soluble in boiling *water*. — It forms with *acids*, neutral and acid salts, which are mostly uncrystallisable. Their solutions are precipitated by ammonia and the fixed alkalis, the solanidine being thrown down in the form of a white jelly. The mono-acid salts have a faintly acid reaction and a bitter acrid taste, and dissolve with difficulty in water and aqueous acids (Zwenger & Kind).

Sulphate of Solanidine.—Both the mono-acid and the bi-acid salt are difficult to isolate, but combine together in varying proportions (Zwenger & Kind).

a. When alcohol containing sulphuric acid is mixed with excess of solanidine, and the strongly acid filtrate is precipitated with ether, the precipitate contains 11·55 p. c. of sulphuric acid, corresponding to a compound of 3 atoms of the mono-acid with 1 atom of the bi-acid salt (by calc. 11·59 p. c. SO^3). When the solution is evaporated in a vacuum or over the water-bath, it becomes turbid from separation of solanidine, after the removal of which there remains a gummy residue.

b. A solution of solanidine in excess of alcoholic sulphuric acid deposits, on evaporation of the alcohol, fine needles containing 12·23 p. c. of sulphuric acid at 100°, which represents a compound of 2 atoms of the mono-acid with 1 atom of the bi-acid salt (by calc. 12·25 p. c. SO^3). On exposure to the air, these crystals lose their water and are converted into a translucent amorphous mass, which again becomes crystalline under water. The crystals dissolve in alcohol, less freely in water, and are thrown down by oil of vitriol as a white precipitate, or from hot solutions as a white resin.

c. The sulphate of solanidine obtained in the decomposition of solanine by sulphuric acid, after being washed, dissolved in alcohol, and precipitated by ether, contains at 100°, 13·11 p. c. of sulphuric acid, or equal numbers of atoms of the mono-acid and bi-acid salts (by calc. 13·11 p. c. SO^3) (Zwenger & Kind).

Hydrochlorate of Solanidine.—Obtained by adding ether to a solution of solanidine in alcoholic hydrochloric acid till turbidity is produced, and allowing the mixture to stand, whereupon crystals make their appearance (Zwenger & Kind). Or by precipitating the above solution with water and crystallising the precipitate from alcohol (O. Gmelin). Rhombic prisms with end-faces and bevelling of the brachydome. Melts with great difficulty. Volatilises undecomposed below its melting-point in white vapours, which condense in crystals.—Dissolves very slightly in water and aqueous hydrochloric acid, easily in alcohol, but is insoluble in ether (Zwenger & Kind).

Dried at 100°.			O. Gmelin. *mean.*	Zwenger & Kind.
50 C	300	73·98	73·82	73 68
N	14	3·45		3 25
40 H	40	9·86	10·18	10·09
Cl	35·5	8·75	8·51	8·82
2 O	16	3·96		4·16
$C^{50}NH^{39}O^{2},HCl$	405·5	100·00		100·00

Nitrate of Solanidine.—This salt is deposited from a solution of solanidine in alcohol containing nitric acid, to which ether has been added in quantity sufficient to produce turbidity. It is converted on standing into fine tufts of prisms having a faintly acid reaction. It is slightly soluble in cold water and is decomposed by boiling water, with separation of solanidine. Dissolves easily in alcohol (Zwenger & Kind).

Chloroplatinate of Solanidine.—Alcoholic hydrochlorate of solanidine is mixed with excess of bichloride of platinum and the mixture is poured into cold water, with constant stirring. The yellow flocks thereby precipitated are washed, dissolved in boiling alcohol, and mixed with sufficient warm water to cause turbidity.—Yellow powder, made up of microscopic globules. It is very slightly soluble in water, but dissolves in alcohol, first becoming soft and transparent (Zwenger & Kind).

	Dried at 100°.		Zwenger & Kind.
50 C	300	52·16	52·00
N	14	2·42	2·38
40 H	40	6·95	7·23
2 O	16	2·81	
3 Cl	106·5	18·51	
Pb	98·7	17·15	16·94
$C^{50}NH^{39}O^{2},HCl,PbCl^{2}$	575·2	100·00	

Solanidine dissolves easily in warm strong *alcohol*, and in cold *ether* (Zwenger & Kind). It is soluble in *benzene* (Kromayer).

Conjugated Compounds of Solanidine.

1. Solanicine.

$$C^{100}N^{2}H^{76}O^{2} = C^{50}NH^{38}O,C^{50}NH^{38}O.$$

ZWENGER & KIND. *Ann. Pharm.* 123, 341.

Formation. By the action of cold strong acids on solanine, the solanidine first formed being partially converted into solanicine, with elimination of water.

Preparation. Solanine is digested with cold fuming hydrochloric acid for four or five days, or until a reddish-brown gummy precipitate of impure solanicine hydrochlorate is deposited. This precipitate is collected and once washed with water, and its alcoholic solution is decomposed with ammonia, which throws down solanicine as a yellow jelly. The crude product thus obtained is washed, dried, triturated, freed from undecomposed solanine and solanidine by boiling with alcohol, afterwards digested with ether, and treated with fresh portions of cold ether, till that liquid remains almost colourless and leaves only a very small quantity of crystalline flocks on evaporation. The solanicine remaining undissolved is purified by dissolving it in alcohol containing hydrochloric acid, precipitating with ammonia, and washing with water.

In this process the ether takes up an amorphous yellow resin, which may be separated from solanicine taken up at the same time by dissolving it in a small quantity of ether. It contains 79·29 to 80·80 p. c. C., 3·13 to 3·40 N., and 10·50 to 10·80 H., and in the platinum-salt 16·83 p. c. of platinum, and has consequently nearly the same composition as solanidine. According to Zwenger and Kind, it is to be regarded as *modified solanidine*. When cautiously heated in a current of carbonic acid, it yields, amongst other products, crystals of solanidine, but forms amorphous salts, easily soluble in water and alcohol. When left to stand in ethereal solution, or when dried at high temperatures, it becomes insoluble in ether, but more easily soluble in alcohol.

Properties. Amorphous pale-yellow mass, translucent in thin layers, obtained from ether in fine needles or yellowish crystalline flocks. Nearly tasteless, and of very faint alkaline reaction.

	Dried at 100°.		Zwenger & Kind. *mean* (4).
50 C	300	83·33	83 01
N	14	3 89	3·87
38 H	38	10·56	10·83
O	8	2·22	2·29
$C^{50}NH^{38}O$	360	100·00	100·00

The formula $C^{50}NH^{39}O$, proposed by Zwenger and Kind, is not admissible, as is shown under solanine. The choice of a formula, therefore, lies between $C^{50}NH^{38}O$ and $C^{50}NH^{40}O$, but the latter requires 82·87 p. c. C., and 11·05 H.; or less carbon and more hydrogen than was found by Zwenger and Kind in three of their analyses. — The formula above given still requires to be doubled (Kr.).

Decompositions. Solanicine turns dark-brown when *heated*, and melts above 250°, with partial decomposition. — It burns with a smoky flame. When submitted to *dry distillation* it yields an empyreumatic oil and charcoal. — It is reddened by strong *acids*, and aqueous solutions of its salts are coloured a fine violet by oil of vitriol dropped into them.

Solanicine is insoluble in *water*. — It forms with *acids*, amorphous reddish-yellow salts, which have a nearly neutral reaction and a bitter acrid taste. Their easily formed deep-yellow solutions in cold water become turbid on boiling, and are precipitated by strong hydrochloric acid. The salts dissolve easily in alcohol, but not in ether.

Hydrochlorate of Solanicine. — Precipitated by ether from a solution of solanicine in absolute alcohol containing hydrochloric acid.

	Dried at 100°.		Zwenger & Kind.
$C^{50}NH^{39}O$	361	91·04	
Cl	35·5	8·96	8·94
$C^{50}NH^{38}O,HCl$	396·5	100·00	

Chloroplatinate of Solanicine. — Bichloride of platinum completely precipitates alcoholic hydrochlorate of solanicine in lemon-yellow flocks on addition of ether.

	Dried at 100°.		Zwenger & Kind. *mean.*
$C^{50}NH^{38}O,HCl,Cl^2$	467·5	82·57	
Pt	98·7	17·43	17·48
$C^{50}NH^{38}O,HCl,PtCl^2$	566·2	100·00	

Hydrochlorate of solanicine forms with *terchloride of gold* a double salt insoluble in water, which decomposes even in the dark.

Solanicine is nearly insoluble in *alcohol*, and requires for its solution 2,000 parts of boiling *ether*.

2. *Glucoside of Solanidine.*

Solanine.

$$C^{86}NH^{69}O^{32} = C^{50}NH^{39}O^{2},3C^{12}H^{10}O^{10}.$$

Desfosses. *Majendie Vorschriften zur Bereitung und Anwendung einiger neuen Arzneimittel.* Leipzig 1822; *J. Pharm.* 6, 375; 7, 414; *N. Tr.* 6. 273; *Berzel. Jahresber.* 2. 114.

Payen & Chevallier. *J. Chim. méd.* 1, 517; *Bull. philom.* 1825, 152.

Peschier. *J. Chim. méd.* 3, 289; *N. Tr.* 14, 2, 269; *Berz. Jahresber.* 8, 248.

O. Henry. *J. Pharm.* 18, 665; *Schw.* 68, 77.

J. Otto. *Ann. Pharm.* 7. 150; 26. 232; *J. pr. Chem.* 1, 58.

Reuling. *Ann. Pharm.* 30. 225; *Berzel. Jahresber.* 20. 324.

Winckler. *Répert.* 76, 384; *Berzel. Jahresber.* 23, 363.—*Jahrb. pr. Pharm.* 4. 143.

Wackenroder. *N. Br. Arch.* 33, 59; *Berzel. Jahresber.* 24, 104.

Baumann. *N. Br. Arch.* 34. 23 and 158; *Berzel. Jahresber.* 24, 408.—*N. Br. Arch.* 35, 137; 38, 292 and 295.

Moitessier. *Compt. rend.* 43, 978; *Instit.* 1856, 411; *Ann. Pharm.* 101, 368; *J. pr. Chem.* 71, 308; *Chem. Centr.* 1857, 124; *Kopp's Jahresber.* 1856, 547.

O. Gmelin. *Ann. Pharm.* 110. 167; *Chem. Centr.* 1859, 567; *Chem. Gaz.* 1859, 385; *Répert. Chim. pure*, 1. 437; *Kopp's Jahresber.* 1859, 402.

Zwenger & Kind. Prelim. notice: *Ann. Pharm.* 109, 244; *Chem. Centr.* 1859, 431; *Kopp's Jahresber.* 1859. 402. Complete: *Ann. Pharm.* 118. 129; abstr. *N. Ann. Chim. Phys.* 63, 377; *Chem. Centr.* 1861, 601; *Kopp's Jahresber.* 1861, 535.—*Ann. Pharm.* 123, 341; *Krit. Zeitschr.* 5. 527; *Chem. Centr.* 1862, 780; *Répert. Chim. pure* 5, 154; *Kopp's Jahresber.* 1862, 382.

A. Kromayer. *N. Br. Arch.* 116, 114; *Chem. Centr.* 1863, 1054; *Kopp's Jahresber.* 1863, 450.

Kletzinsky. *Mittheilungen aus dem Laboraturium.* Wien 1865; abstr. *Zeitschr.* f. Chem. [2] 127.

Discovered by Desfosses, in 1821, in *Solanum nigrum* and *S. Dulcamara*, and by Baup in the shoots of the potato. The alkaloïd from the latter source (the identity of which with that of Desfosses is questionable) has been investigated chiefly by Otto, and more recently by Zwenger and Kind. It was found to be a conjugated sugar-compound by O. Gmelin and by Zwenger and Kind simultaneously.

Source. In potatoes, existing in smaller quantity in the tubers than in the shoots (Baup, *Ann. Chim. Phys.* 31, 109). Most abundantly in the two-inch shoots, also in the herb and tubers, but not in the peel (Otto). According to Heumann (*Repert.* 74, 125) it is found in the unripe green fruits of the potato, but according to Desfosses it is not. 10,000 parts of the following substances contain the accompanying amounts of solanine: potato herb, 0·67; tubers in July, 0·05 pt.

(Baumann); diseased tubers, 0·27 pt. (Wackenroder and Weber, *N. Br. Arch.* 48, 157); healthy tubers, 1·5 pt., amorphous; shoots, 6·8 parts crystalline (J. Wolff, *Pharm. Viertelj.* 2, 503). Old and new potatoes contain solanine even after the complete removal of the eyes. The amount in 10,000 parts (*a*) on the 1st of May, and (*b*) on the 1st of July, is as follows: whole potatoes (*b*) 7·4 parts; without the eyes, (*a*) 3·2, (*b*) 4·2 parts; potato-peel (*a*) 3·6, (*b*) 4·8; peeled potatoes (*a*) 2·4, (*b*) 3·2 parts (Haaf, *N. Repert.* 13, 560; *Chem. Centr.* 1865, 749). These statements require confirmation (Kr.). — Solanine volatilises with the water in which potatoes are boiled (Baumann), and occurs undecomposed in the still-refuse from which potato-spirit has been distilled (Otto). See also Michaelis (*N. Br. Arch.* 13, 233).

Solanine occurs in the berries, but not in the leaves, of *Solanum nigrum*; in the berries, leaves, and stalks of *Solanum Dulcamara* (Desfosses; Henry), and of *S. verbascifolium* (Payen and Chevallier); in *S. mammosum* [especially in the berries (Morin, *J. Chim. méd.* 1, 84)] and *S. ferox*, but not in European species (Pelletier, *J. Pharm.* 14, 256).

According to Winckler, solanine from the stalks of *Solanum Dulcamara* differs from that of potatoes. The former is said to be amorphous, soluble in absolute alcohol, and in nearly all proportions of 80 p. c. alcohol, and when dissolved in hydrochloric acid to give a white precipitate with mercuric chloride, whereas the solanine obtained from potato-shoots is crystalline, sparingly soluble in cold, and more freely in hot alcohol, and does not precipitate mercuric chloride. Hassold made similar observations (*Répert.* 94, 70). Wittstein, however, obtained from dulcamara stalks, ordinary, though amorphous solanine. Heumann found the solanine of green potato-seeds to resemble that of the berries of *Solanum nigrum*; but according to Moitessier, the bases obtained from *Solanum nigrum*, *S. Dulcamara*, and *S. tuberosum* differ greatly. Moitessier's statements respecting solanine from dulcamara were not confirmed by O. Gmelin's examination of potato solanine; moreover, the latter chemist, who had previously obtained ordinary solanine from potato-shoots, afterwards obtained from these shoots, and from the berries of *Solanum Dulcamara* and *S. nigrum*, indistinctly crystalline substances, differing in composition from ordinary solanine, and yielding with sulphuric acid a much smaller quantity of sugar. But inasmuch as all these statements were made before solanidine was sufficiently known, and as potato-shoots yield, sometimes crystalline, sometimes amorphous solanine, the subject requires further investigation.

Pfaff (*Mater. méd.* 6, 505) described as *picroglycion* that portion of the aqueous extract of bitter-sweet stalks which is soluble in alcohol; probably a mixture of solanine and sugar. The *dulcamarin* of Blitz (*N. Tr.* 18, 1, 197) is a similar mixture. — Spatzier's solanine from potato-sap (*Schw.* 61, 311) is phosphate of ammonia and magnesia (Dobereiner, *Schw.* 62, 99), with about 1 p. c. of solanine (Buchner, *Répert.* 48, 337). — Vauquelin (*J. Phys.* 85, 113) obtained a *potato-resin*. On the acid of potatoes, Peschier's *solanic acid*, see x, 207.

Preparation. From fresh Potato-shoots, not too much developed. 1. The comminuted shoots are exhausted with water slightly acidified with sulphuric acid; the acid liquid is supersaturated with ammonia and heated to boiling; and the precipitate thereby formed is ~~collected~~, dried, powdered, and washed with water so long as ~~it~~ gives up colouring matter. The residue is purified by dissolving it in common vinegar, neutralising the solution with ammonia, and boiling. The precipitate is collected, washed, powdered, and boiled for a few minutes with 60 times its weight of 85 p. c. alcohol. The pale-brown liquid, filtered while hot, solidifies to a jelly on cooling, whilst the residue on the filter, when again boiled with an equal quantity of alcohol, yields a colourless filtrate, which deposits crystals on standing for a few minutes. The jelly first obtained is washed with ammonia-water so long as the liquid is coloured, then heated to boiling with alcohol, and allowed to cool on a sand-bath heated to 50°. The crystals of solanine deposited after standing for 24 hours, together with those previously obtained, are purified by washing with alcohol (Reuling; Zwenger & Kind).— 2. Fresh shoots, whole, are digested for 24 hours in water acidified with sulphuric acid, the liquid is decanted, and the now tasteless residue is pressed. The liquid thus obtained is concentrated by digesting in it a fresh portion of the shoots, then strained, and mixed with hydrate of lime to alkaline reaction. The precipitate thereby produced is dried and powdered, and the solanine is extracted from it by repeated boiling with alcohol (Wackenroder). Baumann employs hydrochloric instead of sulphuric acid. If the lime be cautiously added, so that in the first place only the free acid is neutralised, the precipitate afterwards formed is nearly free from sulphate of lime (Meurer, *N. Br. Arch.* 40, 276).

3. The fresh shoots, bruised, are exhausted with hot water containing sulphuric acid; the extract is precipitated with neutral acetate of lead; excess of lead is removed by means of sulphuric acid; and the hot filtrate is precipitated with milk of lime. From this precipitate the solanine is extracted by repeated boiling with alcohol, the crystals deposited from the first decoction being less pure than those obtained afterwards (Otto). In this way Otto obtained in his earlier experiments crystallised solanine, but subsequently only a gelatinous solanine, which could not be made to crystallise. According to Reuling, however, the conversion of the jelly into crystals is effected by washing with aqueous ammonia; and, according to Wackenroder, by dissolving the jelly in sulphuric acid and precipitating with lime.

Inasmuch as solanine prepared with acids may contain solanidine, it must be purified by dissolving it in cold, moderately strong hydrochloric acid, which leaves solanidine undissolved as hydrochlorate (Zwenger & Kind). Or solanine, free from solanidine, may be obtained by beating potato-shoots to a pulp, expressing, precipitating the liquid with milk of lime, and exhausting the precipitate with boiling alcohol. By exhausting the expressed shoots with water containing sulphuric acid, a gelatinous mixture of solanine and solanidine is obtained, from which solanidine may be prepared by boiling with hydrochloric acid (Kromayer).

Desfosses precipitates the filtered juice of the berries of *Solanum nigrum* with ammonia, washes the grey precipitate with cold water, boils it with alcohol, and obtains the solanine partly by cooling, partly by evaporating the alcoholic liquid.—Payen & Chevallier boil the bruised dry berries of *Solanum verbascifolium* with alcohol, evaporate the decoction, dissolve the extract in water, wash the resin which separates, and precipitate the solanine from the aqueous liquid by digesting it with magnesia. From this precipitate the solanine is extracted by boiling alcohol.—Heintz exhausts the powdered stalks of bitter-sweet with alcohol containing sulphuric acid, digests the tincture with lime, filters, distils off the alcohol, washes the residue with water.

dissolves it in dilute sulphuric acid, and precipitates with ammonia. The solanine is extracted from the precipitate by alcohol, and is then to be freed from leaf-green by means of ether.

Properties. White, opaque, somewhat pearly powder (Desfosses). Very delicate, colourless, silky needles, appearing under the microscope as four-sided rectangular prisms (Zwenger & Kind; Payen & Chevallier). It turns yellow when heated, and melts at 235° (Zwenger & Kind) [above 100° (Desfosses)] to a lemon-yellow mass, which solidifies in the amorphous state on cooling. Inodorous. Tastes faintly bitter, and rather burning (Zwenger & Kind); somewhat acrid (Otto). In animals it causes vomiting and afterwards sleep (Desfosses). It is an acrid narcotic poison; one grain killed a rabbit in 6 hours, and 3 grains a larger rabbit in 9 hours, producing paralysis of the hinder extremities (Otto). See also Baumann, who found solanine to act powerfully, but not fatally. — Has a faintly alkaline reaction. — On the microscopic detection of solanine see Erhard (*N. Jahrb. Pharm.* 26, 129).

	Dried in a vacuum. or at 130°.		Blanchet. *mean.*	Moitessier.	O. Gmelin. *mean.*	Zwenger. & Kind. *mean.*
86 C	516	60·35	61·14	60·79	62·19	60·01
N	14	1·63		3·61		1·37
69 H	69	8·07	8·90	8·51	8·72	8·40
32 O	256	29·95		27 09		30·22
$C^{86}NH^{69}O^{32}$	855	100·00		100·00		100·00

Earlier formulæ: $C^{84}NH^{68}O^{28}$ (Blanchet); $C^{42}NH^{35}O^{14}$ (Moitessier); $C^{88}H^{72}O^{30}$ (O. Gmelin); $C^{40}H^{32}O^{14}$ (Delffs, *N. Jahrb. Pharm.* 11, 356). O. Gmelin doubts the fact of solanine containing nitrogen. — The above formula contains 1 atom of hydrogen less than that of Zwenger & Kind, $C^{85}NH^{70}O^{32}$, which is not admissible, because the sum of the hydrogen and nitrogen atoms is an uneven number. If solanine contained 71 atoms of hydrogen (calc. 60·21 p. c. C, 8·28 H.) solanicine would contain 40 atoms of hydrogen, an amount which appears from Zwenger & Kind's analyses of that body to be improbable. These considerations lead to the adoption of the formula for solanine given above (Kr.).

Decompositions. 1. Solanine undergoes decomposition when *heated* above its melting-point, evolving an odour of caramel, and yielding a crystalline sublimate of solanidine. When submitted to rapid dry distillation, it yields an acid viscid distillate, holding solanidine in solution (Zwenger & Kind). When cautiously heated on platinum-foil, covered with an object-holder in the manner described under strychnine (xvii, 483), solanine yields a sublimate which is at first mostly crystalline, but afterwards granular. The crystals consist of delicate tufts of needles, which are not affected by pure water or by water containing ammonia, and are not dissolved by hydrochloric acid, but partially converted into octahedra by prolonged contact with the latter reagent (Helwig, *Anal. Zeitschr.* 3, 55). — 2. When heated in the air, solanine *burns* with smoky flame, leaving porous, easily combustible charcoal (Zwenger & Kind).

3. Solanine heated or boiled with *dilute hydrochloric* or *sulphuric acid*, breaks up into dextroglucose, which remains in solution, and solanidine, which crystallises out as hydrochlorate or sulphate:

$$C^{86}NH^{69}O^{32} + 6HO = C^{50}NH^{39}O^{2} + 3C^{12}H^{12}O^{12}$$ (Zwenger & Kind).

One hundred parts of solanine yield 65·3 parts of sugar (O. Gmelin) (by calc. 63·1 parts $C^{12}H^{12}O^{12}$). Sometimes the solanidine salt is deposited in the form of a resin, which turns crystalline under water. The same splitting up is effected by oxalic, but not by acetic acid (Zwenger & Kind).

Less dilute acids, acting in the cold, produce solanicine and modified solanidine, instead of solanidine, the originally clear solution depositing a yellowish precipitate, and acquiring a fine red, afterwards yellow colour (Zwenger & Kind).

4. Solanine dissolves easily in strong *nitric acid*, forming a colourless solution, which acquires on standing a fine bluish-red colour [rose-red, then brown (Wackenroder)], and afterwards deposits a brown resin. With hot nitric acid it evolves nitric oxide and dissolves to a yellow liquid, from which white crystals afterwards separate (Zwenger & Kind). When solanine is moistened, first with red fuming nitric acid, then with ammonia, a rose-red coloration is produced, which disappears in a few hours (Clarus). — 5. *Oil of vitriol* forms with solanine a reddish-yellow solution, which turns purple-violet on standing, afterwards throwing down a brown powder and losing its colour (Wackenroder). — 6. *Chromic acid* colours solanine sky-blue, gradually changing to green (Clarus).

7. Solanine acquires a fine brown colour in *vapour of iodine*, and forms with it a mass which is soluble with brown colour in water, and may also be obtained by triturating the two substances together. Iodine-water turns aqueous sulphate of solanine brown, without forming a precipitate (Otto). Alcoholic solanine decolorises a small quantity of iodine-water, but is turned of a deep red-brown colour by a larger quantity, but, in the absence of solanidine, without formation of a precipitate (Kromayer). When a solution of iodine in alcoholic solanine is evaporated, there remains an amorphous brown mass, which gives off iodine only when strongly heated, colours alcohol and ether but slightly, and is insoluble in water: Baumann's *iodosolanine.*

8. The dark-yellow solution of *bromine* in alcoholic solanine gives a white flocculent precipitate with ammonia; it leaves on evaporation a black-brown, amorphous mass, soluble in boiling water and in alcohol, but not in cold water or ether (Baumann). — 9. Solanine dissolves in *chlorine-water* to a colourless liquid, which is not precipitated by ammonia (Heumann). Freshly-precipitated solanine, suspended in weak spirit, is not completely dissolved even by a prolonged current of chlorine gas. The filtered liquid gives with ammonia a white precipitate resembling precipitated solanine in appearance, and when evaporated leaves a black-brown, amorphous residue, containing hydrochloric acid, easily soluble in water and alcohol, but insoluble in ether (Baumann).

10. Solanine moistened with water and mixed with 2 parts of solid *sodium-amalgam*, evolves on standing, an odour of nicotine, and yields a distillate containing that substance; in the residue, sulphuric acid sets free butyric acid. Solanine undergoes a similar decomposition when digested with chalk, cheese, and sugar, or with peritoneal membrane and sugar (Kletzinsky).

Kletzinsky obtained a quantity of nicotine amounting to 15 p. c. of the solanine employed (containing 74·06 p. c. C., 17·28 N., and 8·64 H., and in the platinum double salt 34·4 p. c. Pt.), together with an equal quantity of butyric acid (containing

54·54 p. c. C., 9·09 H., and 36·37 O; in the silver-salt 55·3 p. c. Ag.). These statements appear to stand greatly in need of confirmation (Kr.).

11. Solanine reduces *nitrate of silver* and *terchloride of gold* when heated therewith (Otto). It is not decomposed by prolonged boiling with *potash-ley*, and does not reduce an *alkaline solution of cupric oxide* on boiling (Zwenger & Kind). — 12. Alcoholic solanine heated with *iodide of ethyl* or *iodide of amyl*, yields, according to Moitessier, hydriodate of ethyl- or amyl-solanine. O. Gmelin found solanine unaltered after heating for a week with iodide of ethyl.

Moitessier's *ethylsolanine*, precipitated by ammonia from the product obtained as above, forms white microscopic bitter crystals, containing 62·6 p. c. C., and 8·85 H. (the body $C^{42}NH^{34}(C^4H^5)O^{14}$ requires 62·58 p. c. C., 8·8 H.). It is insoluble in water, but soluble in alcohol, and yields poisonous amorphous salts. When heated with iodide of amyl, it yields *ethylamylsolanine*, which, like *amylsolanine*, resembles the ethyl-compound. The solanine employed in these experiments was obtained from dulcamara stalks.

Combinations. — *With Water.* — A. *Hydrated Solanine?* Otto's solanine contained about 10 p. c. of water of crystallisation (Blanchet). The amorphous solanine sometimes obtained, instead of the crystalline, from alcoholic solutions, is a hydrate (Wackenroder).

B. *Aqueous solution.* — Solanine is insoluble in cold, but soluble in 8,000 parts [5,000 parts (Otto)] of boiling water (Desfosses).

With Acids. — Solanine neutralises acids completely, forming mono- and bi-acid salts (Zwenger & Kind). The salts (including those of dulcamara solanine) are for the most part amorphous and gummy. Their taste is bitter and intensely burning (Zwenger & Kind), very repulsive, acrid (Otto). Their clear solution in a small quantity of water becomes turbid when warmed (or diluted), from separation of solanine, which often re-dissolves on cooling. They dissolve in alcohol, from which they are precipitated by ether. They are obtained in the pure state by evaporation, only in the entire absence of free acid, as otherwise salts of solanidine are formed (Zwenger & Kind). — Ammonia and the fixed alkalis throw down from them, after some time, the whole of the solanine as a white gelatinous precipitate, which dries up to a horny mass in the air (Zwenger & Kind). The precipitate produced by ammonia in strong solutions is gelatinous: that produced after some time in dilute solutions, is crystalline. Potash and carbonate of ammonia also throw down crystalline precipitates (Otto). Tartaric acid does not prevent the precipitation (Clarus). According to Baumann, chloride of sodium, sal-ammoniac, sulphate of soda, and many other salts produce white pulverulent precipitates in salts of solanine. The acetates of lead give no precipitate.

Phosphate of Solanine. — Phosphate of soda throws down from sulphate of solanine a white, sparingly soluble, crystalline powder (Otto). The air-dried crystals contains 7·83 p. c. of phosphoric acid (Kletzinsky).

Sulphate of Solanine. — Pearly crystalline mass (Payen & Chevallier). Obtained as a granular crystalline mass, easily soluble in cold water and decomposed by hot water, by dissolving solanine in warm dilute sulphuric acid. With more sulphuric acid a gum is produced (Otto). Was solanidine formed in this case? (Kr.).

A. *Mono-acid.* — Obtained by adding excess of solanine to a solution of B in cold water, and evaporating in a vacuum. — Colourless gum, of faint acid reaction, decomposed by water with separation of solanine (Zwenger & Kind).

	Dried at 100°.		Zwenger & Kind.
86 C	516	57·08	57·13
N	14	1·54	1·27
70 H	70	7·74	8·16
33 O	264	29·20	28·77
SO^3	40	4·44	4·67
$C^{86}NH^{69}O^{32},HO,SO^3$.	904	100·00	100·00

B. *Bi-acid.* — Precipitated by ether from a solution of solanine in alcohol containing sulphuric acid, in the form of a white jelly. — Amorphous, transparent, strongly acid mass, easily soluble in water, and not decomposed by boiling water (Zwenger & Kind).

	Dried in a vacuum.		Zwenger & Kind.
86 C	516	54·14	53·68
N	14	1·47	
71 H	71	7·45	8·00
34 O	272	28·54	
2 SO^3	80	8·40	8·78
$C^{86}NH^{69}O^{32},2(HO,SO^3)$	953	100·00	

Iodide of potassium throws down a crystalline precipitate from sulphate of solanine, after some hours only (Otto). — Solanine crystallises unaltered from aqueous *perchloric acid* (Bödeker).

Hydrochlorate of Solanine. — One hundred parts of solanine take up 4·23 parts of hydrochloric acid gas (Blanchet) (? 1 at. = 4·27 parts HCl); 12·2 parts of hydrochloric acid, but the product is coloured (O. Gmelin). — The salt is obtained by precipitating with ether a solution of solanine in alcohol containing hydrochloric acid, and freeing the precipitate from excess of acid by repeatedly dissolving it in alcohol and precipitating with ether. — Gelatinous precipitate, which dries up to a colourless, transparent, friable gum. — Decomposed with difficulty by boiling with water (Zwenger & Kind).

	Dried in vacuum.		Zwenger & Kind.
86 C	516	57·88	57·86
N	14	1·56	1·30
70 H	70	7·85	8·39
32 O	256	28·74	28·35
Cl	35·5	3·97	4·10
$C^{86}NH^{69}O^{32},HCl$	891·5	100·00	100·00

Solanine forms no salt with *nitric acid,* on account of its being decomposed thereby (Baumann).

Chromate of potash throws down from sulphate of solanine a yellowish precipitate (Otto). — *Phospho-molybdic acid* precipitates solanine lemon-yellow and pulverulent (Sonnenschein; O. Gmelin). — Solanine dissolves in aqueous *ferric chloride,* without affecting the yellow colour (Henmann). — *Stannous chloride* throws down from sulphate of solanine a white jelly; *sulphate of copper* a slight bluish-white pulverulent precipitate (Baumann). — *Mercuric chloride* produces a white precipitate in sulphate of solanine (Otto), but not in the hydrochlorate (v. Planta); *mercuric nitrate* gives a white crystalline precipitate (Baumann). *Iodomercurate of potassium* throws down white slimy flocks from hydrochlorate of solanine (v. Planta, Delffs).

Chloroplatinate of Solanine. — Obtained by adding excess of bichloride of platinum to a solution of solanine in alcohol containing hydrochloric acid, precipitating with ether, and purifying the precipitate from adhering chloride of platinum by oft-repeated solution in alcohol and precipitation with ether. — Faint yellow flocks, which dry up in a vacuum to a dark-yellow, amorphous, transparent, hygroscopic mass. Slightly acid; easily soluble without decomposition in boiling water, and more freely in alcohol (Zwenger & Kind).

	Dried at 100°.		Zwenger & Kind.
86 C	516	48·62	48·10
N	14	1·31	1·26
70 H	70	6·59	7·25
32 O	256	24·14	
3 Cl	106·5	10·03	
Pt	98·7	9·31	9·40
$C^{86}NH^{69}O^{32},HCl,PtCl^2$	1061·2	100·00	

Solanine is not precipitated by *terchloride of gold*, or by *chloride of iridium and sodium* (v. Planta).

Formate and *hydrocyanate of solanine* are amorphous, gummy substances, decomposible by water. The hydrocyanate is sparingly soluble in water (Baumann). — *Ferrocyanide of potassium* precipitates a white powder from sulphate of solanine on standing (Otto). *Sulphocyanide of potassium* throws down yellowish flocks from concentrated hydrochlorate of solanine (v. Planta). — Hydrochlorate of solanine forms no compound with *mercuric cyanide* (Kohl & Swoboda).

Acetate of Solanine. — The easily formed solution of solanine in acetic acid gives off acetic acid on exposure to the air, even when saturated as fully as possible with solanine, leaving a colourless gummy mass, which is no longer quite soluble in alcohol. By evaporating the solution, with repeated addition of water, the whole of the acetic acid is expelled; moreover, ether throws down from the alcoholic solution solanine free from acetic acid (Zwenger & Kind). The neutral solution curdles when evaporated, from the separation of flocks, which re-dissolve on cooling (Heumann).

Oxalate of Solanine. — Oxalic acid produces a crystalline precipitate in sulphate of solanine (Baumann). Oxalate of potash throws down a slight pulverulent precipitate, which afterwards turns crystalline (Otto).

Neutral salt. —When excess of solanine is digested in aqueous oxalic acid, and the filtrate is evaporated in a vacuum, the residue consists of hard white crusts, made up of microscopic needles, often accompanied by an amorphous anhydrous salt. The crusts lose 6·16 p. c. of water at 100° (14 atoms = 6·53 p. c. HO). They dissolve easily in cold water, and deposit solanine in boiling water, the base being re-dissolved on cooling (Zwenger & Kind).

	Dried.			Zwenger & Kind.
$2(C^{86}NH^{69}O^{32},HO)$	1728		96·0	
C^4O^6	72		4·0	4·36
$2C^{86}NH^{69}O^{32},C^4H^2O^8$	1880		100·0	

Solanine forms with *mellitic acid* a neutral salt, the solution of which decomposes on evaporation (Karmrodt).—Solanine added to hot aqueous *succinic acid* and evaporated, yields colourless translucent needles, having an acid reaction, and easily soluble in cold water (Baumann).—It forms with tartaric, racemic, and malic acids, colourless amorphous salts; with mucic acid a neutral salt crystallising in tufts of white needles, easily soluble in water, obtained by adding solanine to a hot aqueous solution.

Picric acid does not precipitate alcoholic solanine (Kemp), but produces sulphur-yellow flocks in the hydrochlorate (v. Planta). *Benzoate of solanine* is amorphous and decomposible by water; the *gallate* is amorphous, and soluble in water, with faint acid reaction (Baumann).—Solanine behaves with *oleic acid* in the same manner as quinine (xvii, 294), (Attfield).

Tannate of Solanine.—Tincture of galls produces white flocks in sulphate of solanine, even when very dilute (Otto). The tincture renders the hydrochlorate turbid, and on addition of a drop of hydrochloric acid, throws down a dense precipitate (v. Planta).—When solanine is added to hot aqueous tannic acid so long as it dissolves, the solution becomes turbid on cooling, and when concentrated deposits tufts of yellow needles, which have an acid reaction, and are sparingly soluble in cold, easily in hot water (Baumann).

Solanine is only slightly soluble in cold, but more freely soluble in boiling *alcohol*, it crystallises from the hot solution on cooling, and from the cold solution on evaporation (Zwenger & Kind). It dissolves in 500 parts of cold, and in 125 parts of boiling alcohol of sp. gr. 0·839; the horny amorphous solanine dissolves very easily in alcohol (Otto). Wackenroder's statement that crystalline solanine becomes gelatinous when boiled with alcohol, or when its cold alcoholic solution is slowly evaporated, was found by Zwenger & Kind to be incorrect.—Solanine dissolves very sparingly in *ether* (Desfosses; Zwenger & Kind); in 4,000 parts of ether (Otto). According to Desfosses, it is insoluble in *oil of turpentine* and *olive oil;* according to Baumann slightly soluble in cold, and perfectly soluble in hot olive oil, which deposits most of it on cooling.

Appendix to Solanine.

Dulcamarine.

WITTSTEIN. *Pharm. Viertelj.* 1, 371, and 495.

An alkaloid occurring, together with solanine, in the stalks of *Solanum Dulcamara.*

Preparation. An aqueous infusion of the stalks of bitter-sweet is mixed with marble and evaporated to an extract, which is exhausted with 90 p. c. alcohol. The tincture is freed from alcohol by distillation. The residue, when kept for some months and diluted with water, deposits granules of lactate of lime, which are removed. The liquid is then carefully neutralized with ammonia, and precipitated with infusion of galls; the precipitate is collected and washed, and mixed while still moist with freshly precipitated oxide of lead. After standing a few hours the liquid is again filtered; and the residue after washing with water is dried, powdered, and boiled with 90 p. c. alcohol. On evaporating the alcoholic solution the dulcamarine is left in white crusts. — The aqueous liquid filtered from the tannate of lead yields a little more dulcamarin by precipitating it with tannic acid and treating the precipitate with oxide of lead and alcohol as before. — Six pounds of bitter-sweet stalks gave 49 grains of dulcamarine.

Properties. Pale-yellow transparent resin, triturable to a yellowish-white powder. When moistened with water or alcohol, and warmed, it smells of bitter-sweet. Tastes bitter, afterwards sweet. — In alcoholic solution it has a weak, though distinct, alkaline reaction.

It loses 8 p. c. of water at 100°, and no more at 120°.

	Dried at 100°.		Wittstein. *mean.*
65 C	390	56·86	57 10
N	14	2·04	2 04
50 H	50	7·29	7·27
29 O	232	33·81	33·59
$C^{65}NH^{50}O^{29}$	686	100·00	100·00

The above is Wittstein's formula, which is inconsistent with the principles of notation adopted in this work.

Decompositions. 1. Dulcamarine *heated* in a tube melts to a yellow liquid, turns brown, then black, and evolves vapours which redden litmus. When heated in a platinum crucible it gives off a faint odour of horn. — 2. Heated with potassium, it yields cyanide of potassium.

It is soluble in 1075 parts of *water*. — It swells up, without dissolving, in *ammonia-water*. Dissolves in *oil of vitriol* with brown-yellow colour, in strong *hydrochloric acid*, in *nitric acid* of sp. gr. 1·2, and in *fuming* nitric acid, from which last it is precipitated by water.

Chloroplatinate of Dulcamarine. — Alcoholic dulcamarine, mixed with hydrochloric acid and bichloride of platinum, throws down a slight yellow precipitate. On evaporating the solution and diluting the residue with water, brownish-yellow flocks are obtained, which, after washing and drying at 100°, contain 11 p. c. of platinum ($C^{65}NH^{50}O^{29}$, $HCl,PtCl^2$ requires 10·98 p. c. Pt).

Dulcamarine dissolves in 10 parts of 90 p. c. *alcohol* at a moderate heat, and in a smaller quantity of the hot liquid. — It is soluble in *acetic acid*, and in 1440 parts of *ether*.

Tannic acid precipitates white flocks from the aqueous, but not from the alcoholic solution.

Kind.

Primary Nucleus $C^{50}H^{42}$; *Oxygen-nucleus* $C^{50}H^{38}O^{4}$.

Hyodyslysin.

$$C^{50}H^{38}O^{6} = C^{50}H^{38}O^{4},O^{2}.$$

STRECKER. *Ann. Pharm.* 70, 188.
VAN HEIJNINGEN & SCHARLÉE. *Scheik Onderz.* 5, 130.

Obtained by boiling hyoglycocholic acid with strong hydrochloric acid for some days, or until the oily layer becomes hard and friable. The product is purified by washing it with boiling water, dissolving in ether, and precipitating with alcohol.

It is insoluble in aqueous ammonia, but soluble in alcoholic potash, and is rendered soluble in water by fusion with hydrate of potash. — It is insoluble in cold, sparingly soluble in boiling alcohol; moderately soluble in ether (Strecker).

Dried at 120°.			Strecker.	Van Heijningen. & Scharlée.
50 C	300	77·72	77·61	78·07
38 H	38	9·84	9·97	9·67
6 O	48	12·44	12·42	12·26
$C^{50}H^{38}O^{6}$	386	100·00	100·00	100·00

Homologous, and according to van Heijningen and Scharlée, identical with dyslysin.

Primary Nucleus $C^{50}H^{44}$; *Oxygen-nucleus* $C^{50}H^{40}O^{4}$.

Hyocholic Acid.

$$C^{50}H^{40}O^{8} = C^{50}H^{40}O^{4},O^{4}.$$

AD. STRECKER. *Ann. Pharm.* 70, 191.

Hyocholalic acid (Strecker). — Formed, together with glycocoll, by boiling hyoglycocholic acid with alkalis. — Also by boiling with acids? (Kr.). See below.

A solution of hyoglycocholic acid in dilute potash-ley is boiled for 24 hours, with addition of water sufficient to retain everything in solution; the solution is decomposed with hydrochloric acid, and the resinous hyocholic acid thereby precipitated is washed with water and dissolved in ether. The ethereal solution, when slowly evaporated, deposits the acid in round, white granules, which sometimes crystallise from alcoholic solution in microscopic six-sided tables.

Dried at 120°.			Strecker. *mean* (4).
50 C	300	74·25	74·27
40 H	40	9·90	10·05
8 O	64	15·85	15·68
$C^{50}H^{40}O^{8}$	404	100·00	100·00

On heating hyoglycocholic acid for half an hour with strong hydrochloric acid, Hoppe (*Chem. Centr.* 1859, 74) obtained a resin soluble in alcohol, which, when decolorised by animal charcoal, rotated a ray of polarised light to the right, $[\alpha]j = 23{\cdot}6°$. This body was designated by Hoppe as *hyocholoïdic acid.* According to his later researches, however, choloidic acid is to be regarded as a mixture of cholic acid and dyslysin, and similar considerations applying to the body now under consideration; the dextro-rotatory action appears, therefore, to belong to hyocholic acid.

Hyocholic acid is nearly insoluble in *water*, but easily soluble in dilute *ammonia* and in dilute *alkalis* and their *carbonates*, from which solutions strong potash-ley precipitates the potash-salt.

Baryta-salt. — Chloride of barium precipitates from the ammonia-salt sparingly soluble flocks, which, after washing with water, are soluble in alcohol. After drying at 160°, the salt loses 1·8 p.c. (= 1 atom) of water at 180°—200°, without undergoing further change.

Dried at 200°.			Strecker.
50 C	300	63·6	63·1
39 H	39	8 3	8·5
7 O	56	11·9	12·5
Ba O	76·5	16·2	15·9
$C^{50}H^{39}BaO^{8}$	471·5	100·0	100·0

Dried at 160°.			Strecker.
50 C	300	62·43	62·27
40 H	40	8·32	8·40
8 O	64	13·33	13·43
BaO	76·5	15·92	15·90
$C^{50}H^{39}BaO^{8}$ + aq.	480·5	100·00	100·00

Hyocholate of ammonia produces flocculent precipitates in salts of *lime*, and of the heavy *metals*.

The acid dissolves freely in *alcohol*, which leaves it in an amorphous state when evaporated. It is less freely soluble in *ether*.

Hyoglycocholic Acid.

$$C^{54}NH^{43}O^{10} = C^{4}NH^{3}O^{2},C^{50}H^{40}O^{8}.$$

Gundelach & Strecker. *Ann. Pharm.* 62, 205; *N. Ann. Chim. Phys.* 22, 38; *Pharm. Centr.* 1847, 881; *N. J. Pharm.* 13, 145; *Kopp's Jahresber.* 1847 and 1848, 913.

Ad. Strecker. *Ann. Pharm.* 70, 179; abstr. *Pharm Centr.* 1849, 660 and 673; *Chem. Gaz.* 1849, 427; *N. J. Pharm.* 16, 450; *Kopp's Jahresber.* 1849, 541.

Van Heijningen & Scharlée. *Scheikund. Onderz.* 5, 105; *Kopp's Jahresber.* 1849, 540.

Discovered by Gundelach & Strecker as the principal constituent of pig's bile, Thénard (*Mem. de Phys. et de Chim. de la Soc. d'Arcueil*, 1, 23) having previously shown that pig's bile is precipitated by acetic acid, and thereby distinguished from ox-bile. Gorup-Besanez (*Ann. Pharm.* 59, 156) had previously regarded the acid of pig's bile as choloïdic acid (p. 52).

Pig's bile contains, besides the above, a small quantity of an acid containing sulphur, *hyotaurocholic acid* [*hyocholeïc acid* (Strecker)], which is decomposed by evaporating its alcoholic solution, with separation of taurine. This body, which has not been isolated, is probably represented by the formula $C^{54}NH^{45}S^2O^{12}$ (corresponding to that of taurocholic acid), and susceptible of being resolved into hyocholic acid and taurine (Strecker). — According to Mulder (*Scheik. Onderz.* 5, 133), pig's bile contains bilin (p. 65), or a similar unstable body, as principal constituent.

The acids of pig's bile exist for the most part in combination with soda, and to a less extent in combination with potash and ammonia (Gundelach & Strecker).

Preparation. A. *Of the Soda Salt.* 1. Fresh pig's bile is digested for some time with Glauber's salt and a small quantity of water. As the Glauber's salt dissolves, hyoglycocholate of soda, colouring matter, and mucus are precipitated. The precipitate is washed with a saturated solution of Glauber's salt by decantation, dried at 100°, and digested with absolute alcohol, which dissolves the hyoglycocholate of soda. The slightly-coloured solution is then decolorised by animal charcoal and mixed with ether, and the precipitate thereby produced is washed with ether, and dried at 100° (Gundelach & Strecker). — 2. Inspissated and powdered pig's bile is digested over the water-bath with absolute alcohol, which leaves mucus undissolved; the tincture is concentrated and placed in the cold; the chloride of sodium which then separates is removed; and the residual solution is decolorised with animal charcoal and mixed with ether, which precipitates hyoglycocholate of soda, whilst cholesterin and fat remain in solution. The resinous precipitate, purified by repeated treatment with ether, still contains chloride of sodium and colouring matter; it is therefore dissolved in cold absolute alcohol, digested with animal charcoal, and again precipitated with ether (Gundelach & Strecker). The product of the second process contains a little potash and ammonia-salt, as well as salt of hyotaurocholic acid.

B. *Separation of the acid from the soda-salt.* — An aqueous solution of the soda-salt is decomposed by hydrochloric or dilute sulphuric acid; the precipitate is dissolved in alcohol and mixed with water, whereby a milky liquid is produced, which deposits oily drops on standing; the liquid is warmed, together with the precipitate, for several days, until the whole of the alcohol is expelled; and the acid thereby precipitated is purified by again dissolving it in alcohol and precipitating with dilute hydrochloric acid (Gundelach & Strecker).

Properties. White, hard, friable resin, melting only above 120°. Has an acid reaction (Gundelach & Strecker). Exerts a slight dextrorotatory action on polarised light $[\alpha]j = 2^\circ$; the soda-salt is optically inactive (F. Hoppe, *Chem. Centr.* 1859, 74).

Dried at 130°.			Gundelach & Strecker. *mean.*	Strecker	v. Heijningen. & Scharlée.	Gorup-Besanez.
54 C	324	70·28	70·08	70·16	69·66	72·36
N	14	3·04	3·54		4·88	
43 H	43	9 33	9·65	9·21	9 53	9·72
10 O	80	17·35	16·73			17·92
$C^{54}NH^{43}O^{10}$.	461	100·00	100·00			

The acid of van Heijningen & Scharlée (according to them $C^{54}NH^{42}O^{11}$) was brown, not completely soluble in aqueous carbonate of soda, and contained 0·69 p. c. S, partly derived (according to Strecker) from the hydrosulphuric acid with which they decomposed the lead-salt suspended in alcohol, and partly from the hyotaurocholic acid with which their product was contaminated.

Homologous with glycocholonic acid (p. 62) (Strecker).

Decompositions. 1. The acid of pig's bile, when *heated* to 140°, is converted into a body resembling dyslysin, containing 77·77 p. c. C., and 10·38 H. (Gorup-Besanez). — 2. It dissolves in warm fuming *nitric acid*, with evolution of red vapours, and yields on distillation oily drops containing nitrocholic acid and volatile fatty acids; the residue contains oxalic acid, cholesteric acid, and a brown colouring matter (Gundelach & Strecker). — 3. The acid is not affected by boiling with *peroxide of lead* and dilute *sulphuric acid;* when heated with sulphuric acid and *bichromate of potash*, it yields hydrocyanic acid and volatile fatty acids. — 4. It dissolves easily in *oil of vitriol*, and is carbonised when heated therewith, evolving sulphurous acid. When hyoglycocholic acid is evaporated with dilute sulphuric acid, a violet coloration, changing to purple, is produced. — 5. When boiled for some time with *hydrochloric acid*, it melts to an oil, which, after boiling for several days, turns viscid, and ultimately nearly solid, losing at the same time its solubility in alcohol and in aqueous ammonia. The ultimate products are hydrochlorate of glycocoll and hyodyslysin, the latter probably being derived from products richer in water formed previously (Strecker).

$$C^{54}NH^{43}O^{10} = C^{50}H^{38}O^{6} + C^{4}NH^{5}O^{4}.$$

6. On boiling with *potash-ley*, it yields hyocholic acid and glycocoll (Strecker). About the melting-point of caustic potash it evolves a little ammonia (Gundelach & Strecker). — 7. Gives the bile-reaction with *oil of vitriol* and *sugar*. — 8. Not decomposed during the putrefaction of pig's bile (Gundelach & Strecker).

Combinations. With Water. Moist hyoglycocholic acid melts at 100°, or in boiling water, to a mass which may be drawn out into silky threads. — It dissolves very slightly in pure water, rather more freely in acidulated water.

With Bases. — The acid combines with bases, and expels carbonic acid from dilute aqueous carbonates of the alkalis. It dissolves easily in aqueous ammonia. The dry acid does not dissolve in potash-ley, but after decanting the potash, it dissolves in water. The salts are represented by the formula $C^{54}NH^{43}O^{10},MO$, or probably $C^{54}NH^{42}MO^{10} + aq$. The hyoglycocholates of the alkalis are almost entirely precipitated from their aqueous solutions by sal-ammoniac, and by hydrochlorates and sulphates of the alkalis. The precipitates generally dissolve on boiling, but reappear on cooling. Hyoglycocholic acid is thrown down from its salts (including those which contain a small quantity of hyotaurocholic acid) as a white sticky resin, by acetic, tartaric, lactic, and mineral acids; dilute solutions are turned milky. — The alcoholic acid does not precipitate metallic salts (Gundelach & Strecker).

Hyoglycocholate of Ammonia. — Precipitated by strong aqueous ammonia-salts from an aqueous solution of hyoglycocholate of soda, in the form of a crystalline powder, which dissolves on warming, and reappears as the solution cools. — Permanent over oil of vitrol. Gives off ammonia at 100°, or when boiled with water. Dissolves easily in water, but with difficulty in aqueous ammonia-salts. Easily soluble in alcohol, from which it is precipitated by ether.

	Dried over oil of vitriol.		Gundelach & Strecker.
54 C	324	66·53	66·1
2 N	28	5·75	5·1
47 H	47	9·65	9·6
11 O	88	18·07	19·2
$C^{54}NH^{43}O^{10},NH^4O$	487	100·00	100·0

Hyoglycocholate of Potash. — Obtained by precipitating a solution of the acid in potash-ley with warm aqueous sulphate of potash, washing with the same liquid the flocks which are deposited on cooling, then drying, dissolving in absolute alcohol, and precipitating with ether. — Or by dissolving the acid in aqueous carbonate of potash, evaporating the solution, exhausting the residue with absolute alcohol, and precipitating with ether. — White amorphous friable mass, which does not become sticky at 120°.

			Gundelach & Strecker. *mean.*
54 C	324	63·76	63·67
N.	14	2·75	
43 H	43	8·46	8·68
10 O	80	15·76	
KO	47·1	9·27	9·21
$C^{44}NH^{43}O^{10},KO$	508·1	100·00	

Hyoglycocholate of Soda. — Preparation, p. 102. — White friable mass, having an intense and persistent bitter taste. — When heated it melts, puffs up, and burns with a bright smoky flame. Dissolves easily in water and in alcohol. The solution in the latter liquid is not precipitated by carbonic acid, and leaves a colourless varnish when evaporated (Gundelach & Strecker).

	Dried at 110°.		Gundelach & Strecker. *mean.* *a.*	 *b.*
54 C	324	65·87	65·54	65·1
N	14	2·84	3·01	3·3
43 H	43	8·72	8·98	8·9
10 O	80	16·27	16·29	16·6
NaO	31	6·30	6·18	6·1
$C^{54}NH^{43}O^{10},NaO$	492	100·00	100·00	100·0

a prepared according to 1; *b* according to 2, with deduction of 0·5 to 1·5 p. c. of chloride of sodium.

Hyoglycocholate of Baryta. — Chloride of barium throws down from the aqueous soda-salt a white, somewhat gelatinous precipitate which dissolves in warm, less freely in cold water, and easily in alcohol. Melts when heated.

	Dried at 110°.		Gundelach & Strecker. *mean.*
54 C	324	60·29	59·71
N	14	2·61	
43 H	43	7·99	8·06
10 O	80	14·90	
BaO	76·4	14·21	14·05
$C^{54}NH^{43}O^{10},BaO$	537·4	100·00	

Hyoglycocholate of Lime. — Precipitated from the soda-salt by chloride of calcium. When the coloured soda-salt (obtained by precipitating alcoholic pig's bile with ether, and re-dissolving the precipitate in water) is employed in the preparation of this compound, the whole of the colouring matter remains in solution on precipitating incompletely with chloride of calcium. — The salt dissolves in water more easily than the baryta-salt, and easily in alcohol, from which it is precipitated by water. Carbonic acid throws down carbonate of lime from the alcoholic solution.

			Gundelach & Strecker.
54 C	324	66·26	65·69
N	14	2·86	3·24
43 H	43	8·79	8·82
10 O	80	16·37	16·47
CaO	28	5·72	5·78
$C^{64}NH^{43}O^{10},CaO$	489	100·00	100·00

The soda-salt gives white flocculent precipitates with *sulphate of magnesia*, *sulphate of manganese*, and *chloride of zinc*.

Hyoglycocholate of Lead. — Neutral acetate of lead throws down from aqueous hyoglycocholate of soda a white, somewhat gelatinous precipitate, which turns flocculent on heating the liquid, and dries up to a soft powder containing 23·1 to 24·4 p. c. of oxide of lead. The liquid is acid after precipitation, and retains in solution a part of the hyoglycocholic acid, which may be precipitated, though not completely, by basic acetate of lead or by ammonia. — The salt dissolves only slightly in water, but is easily soluble in alcohol, forming an alkaline solution from which it is precipitated by ether (Gundelach and Strecker).

On mixing an alcoholic solution of pig's bile, free from mucus, with alcoholic neutral acetate of lead, removing the dark-brown precipitate thereby produced, adding to the filtrate more alcohol to throw down yellow colouring matter, filtering again, evaporating to one-third, and mixing with water, a lead-salt is precipitated which forms Van Heijningen and Scharlée's *fellonate of lead.* According to Strecker, it is a mixture of a large quantity of hyoglycocholate with a little hyotaurocholate of lead. It remains pulverulent at 130°.

	Dried at 130°.		Van Heijningen. & Scharlée.
54 C	324	56·54	56·04
N	14	2·44	2·93
43 H	43	7·50	7·52
10 O	80	13·96	14·01
PbO	112	19·56	19·50
$C^{54}NH^{43}O^{10},PbO$	573	100·00	100·00

Contained also 0·31 p. c. of sulphur.

The aqueous soda-salt gives with *ferric chloride* yellowish-white flocks, which turn red-brown on boiling; with *copper-salts* a bluish-white precipitate; with *mercuric chloride* a white, and with *mercurous nitrate* a gelatinous precipitate (Gundelach and Strecker).

Hyoglycocholate of Silver.—Precipitated from the soda-salt by nitrate of silver not in excess.—White precipitate, soluble with difficulty in boiling water and more easily in alcohol.

			Gundelach & Strecker.
54 C	324	56·15	56·13
N	14	2·42	
43 H	43	7·45	7·61
11 O	88	15·26	
Ag	108	18·72	18·61
$C^{54}NH^{43}O^{10},AgO$	577	100·00	

The acid dissolves easily in *alcohol*, and to a slight extent in *ether*.

Primary Nucleus $C^{50}H^{50}$.

Hyænic Acid.

$$C^{50}H^{50}O^4 = C^{50}H^{50},O^4.$$

L. Carius. *Ann. Pharm.* 129, 168; *Krit. Zeitschr.* 6, 622; *Kopp's Jahresber.* 1863, 335.

Occurs, together with palmitin and olein, as a glyceride, in the fat of the anal glandular pouches of *Hyæna stricta.*

The fat is saponified with baryta-water or soda-ley; the soap is decomposed; and the liberated acids are dissolved in twice their volume of hot absolute alcohol and set aside for some days, when the deposit is collected, strongly pressed, and recrystallised from alcohol. The alcoholic mother-liquor acidified with acetic acid, yields, on addition of hot neutral acetate of lead, a further quantity of the acid as lead-salt, together with palmitate of lead, whilst oleate of lead remains in solution. The precipitate is decomposed by digestion with very dilute nitric acid, and the mixed acids thus set free are allowed to crystallise from alcohol, the greater part of the palmitic acid then remaining in solution. The whole of the crystals obtained are then freed from palmitic acid by fractional precipitation with acetate of lead according to Heintz's process (xvi, 210, 354). The lead-salts precipitated first are exhausted repeatedly with hot alcohol, and then decomposed with nitric acid, and the hyænic acid thus liberated is recrystallised from absolute alcohol.

Properties. Hyænic acid crystallises from alcohol in granules consisting of microscopic curved needles, and from ether in more distinct crystals. It melts at 77° to 78°, but softens at a lower temperature; at 75° it is semifluid and pasty. After fusion it solidifies to a hard, crystalline, friable mass. It has an acid reaction.

			Schacht. *mean.*
50 C	300	78·52	78·47
50 H	50	13·09	13·27
4 O	32	8·39	8·26
$C^{50}H^{50}O^4$	382	100·00	100·00

The acid cannot be resolved into portions of different composition by fractional precipitation with neutral acetate of lead (Carius).

The *hyænates of the alkalis* are very hard soaps, soluble in a small quantity of warm water, and decomposible by a larger quantity, with precipitation of acid salt. — The insoluble salts are not (completely) decomposed by acetic acid. When heated with a large quantity of water, they give up a portion of the base. In preparing them, therefore, the precipitates produced by acetates of the bases in the hot alcoholic acid, are washed first with alcohol and afterwards with a small quantity of water.

Hyænate of Lime. — White, microscopic needles, melting at 85° to 90°. The salt dissolves very sparingly in boiling absolute alcohol.

			Schacht.
50 C	300	74·82	74·69
49 H	49	12·22	12·43
Ca	20	4·99	4·80
4 O	32	7·97	8·08
$C^{50}H^{49}CaO^4$	401	100·00	100·00

Hyænate of Lead. — White, very bulky precipitate, which cakes together in boiling absolute alcohol, dissolving to a very slight extent, and crystallising in microscopic scales on cooling.

			Schacht.
50 C	300	61·89	61·73
49 H	49	10·11	10·04
Pb.	103·5	21·39	21·15
4 O	32	6·61	7·08
$C^{50}H^{49}PbO^4$	481·5	100·00	100·00

COMPOUNDS CONTAINING 52 ATOMS OF CARBON.

Primary Nucleus $C^{52}H^{42}$.

Cholesterilin.

$C^{52}H^{42}$.

ZWENGER. *Ann. Pharm.* 66, 5.

Obtained in three modifications, as alpha-, beta-, and gamma-cholesterilin, by the action of sulphuric acid on cholesterin.

Cholesterin is added to a mixture of oil of vitriol with half its volume of water at a temperature of 60° to 70°, and more oil of vitriol is added till the mass becomes soft and dark-red. The whole is then mixed with a large quantity of water, and the hydrocarbons thereby precipitated are washed with water and subsequently boiled with ether so long as that liquid continues to take up colouring matter, or to dissolve anything of importance. Beta- and gamma-cholesterilin are thus dissolved, together with a small quantity of alpha-cholesterilin, the principal part of which, however, remains undissolved. The ethereal solution is mixed with alcohol, whereby the cholesterilin is precipitated, whilst unchanged cholesterin remains in solution; the yellow resinous precipitate is dissolved in ether, any residual alpha-cholesterin being separated; and the ethereal solution is allowed to evaporate spontaneously, whereupon it first deposits crystals of beta-cholesterilin, and afterwards a resinous mass of gamma-cholesterilin.

Alpha-cholesterilin. — Whitish-yellow earthy mass, which may be obtained from its solution in turpentine-oil in delicate faintly lustrous crystals. Inodorous and tasteless; lighter than water (Zwenger). The (probably too dilute) solution in coal oil is optically inactive (Hoppe-Seyler). — It turns yellow when heated, melts at about 240°, being for the most part decomposed, and solidifies to a yellow glass on cooling. — In contact with nitric acid it puffs up, and is apparently converted into cholesteric acid (xiii, 157). — It forms with oil of vitriol a soft, brown-red resin, from which it is separated by water nearly unaltered. A solution of this resin in a larger quantity of oil of vitriol is of a dirty dark-green colour by reflected, and dark-brown by transmitted light. — It is decomposed by chlorine.

Alpha-cholesterilin is insoluble in water, and nearly insoluble in alcohol. It dissolves slightly in boiling ether, crystallising on cooling. It is soluble in warm volatile oils.

2. *Beta-cholesterilin.* — Formed only in small quantity. — Highly lustrous white laminæ, or needles. Melts at about 255° to a colourless liquid, which solidifies in a radiated crystalline mass; when slowly heated it is yellow and uncrystallisable, and gives off a volatile oil (Zwenger). Exerts a dextrorotatory action on polarized light (Hoppe-Seyler). — Oil of vitriol converts it into a dark-red resin, a solution of which in excess of sulphuric acid appears of an emerald-green colour, afterwards dark-green by reflected, and dark-red by transmitted light. — It dissolves with difficulty in warm ether, but easily in warm oils, either fixed or volatile.

3. *Gamma-cholesterilin.* — Purified by again dissolving in ether and precipitating with alcohol. — Yellow amorphous resin, or yellowish-white powder, melting at 127°, and solidifying to a brittle glassy mass on cooling (Zwenger). Dextro-rotatory (Hoppe-Seyler). — Yields by dry distillation a volatile oil of aromatic odour. Dissolves with difficulty in alcohol, easily in cold ether, and easily in warm oils, either fixed or volatile.

			Zwenger. *mean.*		
			α.	*β.*	*γ.*
52 C	312	88·13	88·05	88·29	87·92
42 H	42	11·87	12·09	12·18	11·99
$C^{52}H^{42}$	354	100·00	100·14	100·47	99·91

Zwenger gives the following formulæ as possible: $\alpha = C^{32}H^{26}$; $\beta = C^{22}H^{18}$; $\gamma = C^{27}H^{22}$; 1 atom of each of the three bodies would then be formed by the breaking up of 1 atom of cholesterin (according to Zwenger $C^{81}H^{69}O^{3}$), with elimination of 3 atoms of water. — He was unable to convert these bodies one into another.

Cholesterone.

$C^{52}H^{42}$.

ZWENGER. *Ann. Pharm.* 69, 347.

Obtained in two different modifications, as alpha- and beta-cholesterone, by the action of hydrated phosphoric acid on cholesterin.

Cholesterin is boiled with 6 or eight parts of strong aqueous phosphoric acid till it melts. Water is then added, and the dirty-white pasty mass which is deposited is washed and boiled with alcohol, to separate the soluble alpha-cholesterone from the insoluble beta-cholesterone. The former is purified by recrystallisation from absolute alcohol, and the latter by dissolving it in boiling ether, and boiling the resulting crystals with alcohol.

Alpha-cholesterone. — Colourless, transparent, highly lustrous, rhombic prisms, often half-an-inch long. Inodorous and tasteless. Melts at 68° to a colourless liquid, which slowly solidifies in a crystalline mass in the cold. When more strongly heated, it boils and distils almost unchanged, yielding a yellow crystalline distillate. — Burns with smoky flame. It is oxidised by nitric acid, coloured red by oil of vitriol, and decomposed by chlorine, with liberation of hydrochloric acid. — It dissolves very sparingly in cold, but much more freely in boiling alcohol; very easily in ether, and in volatile and fixed oils.

Beta-cholesterone. — Very delicate, white, somewhat silky needles, melting at 175°, and solidifying to a brittle crystalline mass on cooling. Distils partially undecomposed. Dissolves very slightly in boiling alcohol and in ether, but easily in volatile and fixed oils.

				Zwenger.
				mean.
52 C	312	88·13	87·70	87·70
42 H	42	11·87	12·12	12·04
$C^{52}H^{42}$	354	100·00	99·82	99·74

Cholesterin.

$C^{52}H^{44}O^{2} = C^{52}H^{42},H^{2}O^{2}$.

CONRADI. *Diss. ex cum calp. fell.* Jena, 1775. — GREN. *Dietrich Diss. contin. duas observ. circa calculos.* Halle 1778. — CRELL. *Beitr. zu den Chem. Ann.* 4, 1, 19. — FOURCROY. *Syst. des conn. chim.* 10, 53. — BOSTOCK. *A. Gehl.* 6, 653. — CHEVREUL. *Ann. Chim.* 95, 5. — *Recherches sur les corps gras*, p. 153. — PLEISCHL. *Merkwürd. Krankheitsgesch.* Prag, 1826, 28; abstr. *Br. Arch.* 21, 34; *Kastn. Arch.* 8, 300. — KUHN. *Dissert. de Cholestearine.* Leipzig, 1828; abstr. *Kastn. Arch.* 13, 337.

Saussure. *Ann. Chim. Phys.* 13, 338; *N. Tr.* 5, 2, 120.

Couerbe. *Ann. Chim. Phys.* 56, 181.

Marchand. *J. pr. Chem.* 16, 37.

Payen. *N. Ann. Chem. Phys.* 1, 58.

Schwendler & Meissner. *Ann. Pharm.* 59, 107; *Berz. Jahresber.* 27, 623.

Gobley. *N. J. Pharm.* 9, 81; *Compt. rend.* 21, 990. — *N. J. Pharm.* 11, 409; 12, 5; *Kopp's Jahresber.* 1847 and 1848, 858. — *N. J. Pharm.* 17, 406; 18, 107; *Kopp's Jahresber.* 1850, 558. — *N. J. Pharm.* 19, 417; *Kopp's Jahresber.* 1851, 598. — *N. J. Pharm.* 21, 246; *Kopp's Jahresber.* 1851, 588. — *N. J. Pharm.* 33, 161; 40, 84; *Kopp's Jahresber.* 1861, 799.

Zwenger. *Ann. Pharm.* 66, 5; *Pharm. Centr.* 1848, 569; *Kopp's Jahresber.* 1847 and 1848, 921. — *Ann. Pharm.* 69, 347; *Pharm. Centr.* 1849, 321; *Kopp's Jahresber.* 1849, 547.

Heintz. *Pogg.* 79, 524; *Pharm. Centr.* 1850, 577; *Ann. Pharm.* 76, 366; *Kopp's Jahresber.* 1850, 574.

Hoppe-Seyler. *Arch. patholog. Anat.* 15, 126; *Chem. Centr.* 1859, 65; *Kopp's Jahresber.* 1858, 567. — *Medicin-chem. Untersuchungen.* I. 140; *Kopp's Jahresber.* 1866, 744.

Berthelot. *Compt. rend.* 47, 262; *N. Ann. Chim. Phys.* 56, 54; *Ann. Pharm.* 112, 356; *J. pr. Chem.* 77, 1; *Kopp's Jahresber.* 1858, 417.

Beneke. *Studien über Vorkommen, Verbreitung, und Function von Gallenbestandtheilen;* Giessen 1862. — *Ann. Pharm.* 122, 249; *Pharm. Viertelj.* 11, 568; *Répert. Chim. pure,* 4, 471; *Chem. Centr.* 1862, 819; *Kopp's Jahresber.* 1862, 507. — *Ann. Pharm.* 127, 105; *Par. Soc. Bull.* 6, 59; *Chem. Centr.* 1864, 15; *Kopp's Jahresber.* 1863, 544.

O. Lindenmeyer. *J. pr. Chem.* 90, 321; *Chem. Centr.* 1864, 412; *N. J. Pharm.* 45, 286; *Kopp's Jahresber.* 1863, 542.

Cholsterin, Cholestearin, Fatty wax of gall-stones, Bile-fat, Gall-stone fat. — Discovered in gall-stones by Conradi in 1775, and by Gren in 1788, and in the vegetable kingdom by Beneke in 1862. See also xvi, 480.

Source. A. *In the animal kingdom.* Cholesterin forms the principal constituent [as much as 97·5 per cent. (Gobley)] of most human gall-stones (*Handbuch* viii, 44), and occurs in smaller quantity in various parts of the body, as a normal, and also as a pathological product, in the latter case often separated in crystals. In the bile (Tiedemann and Gmelin, *Handbuch* viii, 39 and 44); in blood (Gmelin & Gugert, ed. 3, 1386. — 1829 !; Denis; Boudet, *Ann. Chim. Phys.* 52, 337) to the extent of 0·1 p. c. (Boudet, *N. J. Pharm.* 6, 338). See *Handbuch* viii, 44, 170, 194, and 207. In the brain (Gmelin [See also Wöhler, *Ann. Pharm.* 41, 238], Couerbe, *Ann. Chim. Phys.* 56, 170) amounting to about one-third of the brain-fat (v. Bibra. *Handbuch* viii, 508, 511); in the spinal cord, and in the crystalline lens (Mettenheimer); abundant in the spleen (Marcet); in yolk of egg (Lecanu, *J. Pharm.* 14, 625; 15, 1; Lehmann, *J. pr. Chem.* 27, 259) to the amount of 0·42 p. c. (Gobley); in the ova of the carp, and the milt of the carp and herring, and in snail's fat (Gobley); in haddock-liver oil (Beneke); in sweat (Schottin); in the intestinal canal of mammals and birds (Tiedemann & Gmelin); in Peruvian guano and other excrements (Hoppe-Seyler).

The fæces of the crocodile contain cholesterin, but no uric acid; those of the boa, uric acid free from cholesterin; those of the herbivora contain no cholesterin (Marcet).

Cholesterin occurs in *Castoreum moscoviticum* (Brandes, *N. Br. Arch.* 1, 183), and in musk (Blondeau & Guibourt).—In pus, in dropsical exudations, in transudations, in the secretions of the sebaceous glands, in calcified and obsolete tubercles, and in many other pathological products.—In human milk to the amount of 0·0318 p. c. (Tolmatscheff, *Kopp's Jahresb.* 1867, 811).

According to Hoppe-Seyler, it occurs, together with protagon, in all the most important organs of the animal and vegetable organism, both these bodies, like the proteides, appearing to take part in the processes going on in the cells; they are found in the nervous tissue, in the yolk of egg, in the seminal fluid of animals, and in the red and colourless corpuscles of the blood.

B. *In the vegetable kingdom.* In peas, beans, and almonds, and consequently in fatty oil of almonds, in olive oil, and probably in all plant seeds, as well as in chlorophyll, and in flower-organs (Beneke). Knop (*Chem. Centr.* 1862, 819) observed spangles of cholesterin deposited from the phosphoretted fat of peas (xvi, 487). Ritthausen (*J. pr. Chem.* 85, 212; 88, 145) obtained from wheat-gluten a laminated fat and oil, with crystals of cholesterin.—The formation of cholesterin in seeds begins early, but is increased greatly at the time of ripening. Dry, unripe peas contain, on an average, 0·025 p. c., dry, ripe peas 0·055 p. c. of cholesterin (Lindenmeyer). The radicles of malt contain cholesterin (Lermer, *Dingl.* 179, 71). Maize contains it to the extent of 0·1 p. c. (Hoppe-Seyler, *Krit. Zeitschr.* 10, 32). It occurs also in young rose-shoots, and in wine-yeast (Hoppe-Seyler, *Jahresb.* 1866, 745).

The carotin and hydrocarotin, described xvi, 14, 53, are regarded by Fröhde and Sorauer (*N. Br. Arch.* 126, 202) as anhydrous and hydrated cholesterin, mixed with colouring matter; they obtained cholesterin from white carrots, and from the seeds, by the process employed for the preparation of carotin. Their view is not reconcileable with Husemann's analysis of carotin, or with his statements as to the behaviour of that body towards alcohol, and of hydrocarotin when heated; Husemann (*N. Br. Arch.* 129, 30) regards it as totally erroneous.

Preparation. From Gall-stones. Gall-stones are powdered and exhausted with boiling water, and afterwards dissolved in boiling alcohol. The filtered solution deposits cholesterin in crystals on cooling. It is purified by recrystallising it from alcohol containing potash, and washing with alcohol and water. Thudichum (*Chem. Soc. Qu. J.* 14, 114; *Anal. Zeitschr.* 1, 122.—*Chem. Soc. J.* [2] 1, 34; *Chem. Centr.* 1863, 846), exhausts gall-stones with benzol, which takes up cholesterin and bile-substances, leaving colouring matter and ash constituents undissolved. The residue left on evaporating the benzol is crystallised from boiling alcohol.

From Ox-bile. The bile, evaporated to a thin extract, is shaken repeatedly with fresh portions of ether; the mixed ethereal liquids are distilled; and the crystals which then separate are purified by pressing and recrystallising them from hot alcohol.—*From brains.* Brain-pulp (xvi, 480) is exhausted with hot alcohol; the precipitate which makes its appearance on cooling is exhausted with ether; and the ethereal liquid is distilled. The red pulpy residue is boiled with alcohol and excess of hydrated oxide of lead, whereby lead-salts of fatty acids are formed, which for the most part remain behind on filtration. The cholesterin crystallises out on cooling, and is purified by again treating its hot alcoholic solution with oxide of lead and recrystallising from alcohol (Müller, *Ann. Pharm.* 105, 363). See also xvi, 480. Beneke obtains cholesterin from yolk of egg in the same manner as from peas.

From dry Peas and other Seeds. The finely pounded seeds are macerated for 48 hours with alcohol mixed with $\frac{1}{4}$th its volume of ether, and afterwards for 24 hours with alcohol and $\frac{1}{8}$th its volume of ether; the extracts are distilled; the residue is suspended in water and shaken with ether; the ethereal layer is separated and distilled; and the residue after boiling for an hour with alcoholic potash, is dried, dissolved in water, and shaken with ether, which takes up cholesterin and a little yellow colouring matter. The product is purified by treating it with weak spirit (Lindenmeyer). Beneke digests 5 pounds of bruised peas for 24 hours in an equal quantity of 94 p. c. alcohol at the temperature of 35°; evaporates the deep-yellow tincture to an extract; boils the extract with 400 cubic centimetres of water and 1 pound of litharge; decants the water; exhausts the lead-precipitate with boiling alcohol; treats the alcoholic liquid with hydrosulphuric acid; then filters and cools, whereupon the cholesterin crystallises. The mother-liquor still contains cholesterin, to obtain which the alcohol is driven off, and the residue boiled for some hours with baryta-water. The flocks thereby formed are separated by filtration and boiled with alcohol. The filtrate deposits, on cooling, crystals of cholesterin, the entire yield of which amounts to 1·5 grammes.

¶ The following process is given by Hoppe-Seyler for the detection and estimation of cholesterin in animal and vegetable tissues and fluids: The substance under examination is repeatedly exhausted with its own volume or several times its volume of ether; the clear decanted or filtered extracts, completely separated from the aqueous solution, are distilled in the water-bath; and the dried residue is weighed. Part or the whole of this residue is then boiled for several hours with a clear concentrated alcoholic solution of potash, and finally the alcohol is evaporated, the residue dissolved in water, and the mobile solution repeatedly shaken up with ether. This ethereal extract contains the cholesterin generally almost pure; in the contrary case, the residue is agitated while yet warm, with dilute potash-ley, and, after cooling, again treated with ether. A small portion of the soaps (produced from saponifiable fats) is then dissolved by the ether, only when there is an insufficient quantity of water and alkali present. By this process the quantities (in grammes) of cholesterin in 100 c.c. of blood were found to be as follows: I and II from very fat young geese, III and IV from a fat old goose, V from an ox.

In the blood-corpuscles.					In the serum.			
I.	II.	III.	IV.	V.	I.	II.	III.	IV.
0·043	0·052	0·040	0·060	0·048	0·234	0·314	0·019	0·035

Hence it appears: 1. That the proportion of cholesterin in the corpuscles is nearly constant, varying only from 0·04 to 0·06 grm. in 100 c.c.;

2. That the proportion in the serum is very variable, rising or falling with that of the fat. ¶

Cholesterin crystallised from alcohol is hydrated (See below). It is freed from water by heat or by fusion.

Properties. Cholesterin crystallises from rock-oil or chloroform in anhydrous silky needles (Lindenmeyer). It melts at 137° (Chevreul) [137·5° (Kühn), 135 to 137° (Boudet), 136 to 137° (Beneke). 145° (Gobley; Lecanu)], to a colourless limpid oil, which solidifies to a satiny crystalline mass on cooling. Out of contact of air [and in presence of air, at the boiling point of mercury (Heintz)] it sublimes almost undecomposed (Chevreul) in delicate laminæ (Kühn).—Sp. gr. 1·067 (Hoppe-Seyler); when fused, 1·03 (Hein). Levorotatory; $[\alpha]\ j = 34°$ (Hoppe-Seyler); $[\alpha]\ D = 31·59°$ (Lindenmeyer). The rotatory power is independent of temperature and strength of solution, and is not altered by standing for two months.

Calculations.

	$C^{48}H^{40}O^2$.	$C^{52}H^{44}O^2$.	$C^{56}H^{48}O^2$.	$C^{60}H^{52}O^2$.
C	83 72	83 87	84 00	84·11
H	11·63	11·83	12 00	12·15
O	4 65	4·30	4·00	3·74
	100·00	100·00	100 00	100·00

Analyses.

	Chevreul.	Couerbe.	Payen.	Marchand.	Heintz.	Kolbe.
C	83·97	83·77	83 84	84·18	83·85	84 10
H	11·88	12·10	11·86	12·03	12·00	12·10
O	4·15	4·13	4·30	3 79	4·15	3 80
	100·00	100·00	100·00	100 00	100·00	100 00

Free from nitrogen, phosphorus, and sulphur (Schwendler & Meissner). The above are analyses of cholesterin from gall-stones, excepting Couerbe's and Kolbe's, the former of whom analysed cholesterin from brains, and the latter cholesterin from peas. Heintz also analysed distilled cholesterin; Marchand, cholesterin from ox-bile, hydrocele, human brains, and the fluid of hydrocephalus; Gobley, that of the milt of carp and herring, the fat of venous human blood, and yolk of egg: Muller, that of brains; and Kolbe, that of yolk of egg. The results of all these analyses approximate to 83·9 p. c. C., 11·9 H., and 4·2 O.; Gobley's analysis alone gave 85·0 p. c. C. and 11·6 H. Cholesterin may, in accordance with these numbers, be represented by any of the above formulæ, or by the intermediate formulæ $C^{50}H^{42}O^2$ [according to which cholesterin would bear the same relation to hyocholic acid ($C^{50}H^{40}O^8$), that alcohol bears to oxalic acid (Berthelot)], $C^{56}H^{16}O^2$, and $C^{58}H^{50}O^2$. The formula $C^{52}H^{44}O^2$, however, adopted by Gerhardt (*Précis*, 2, 425), is generally accepted, and agrees sufficiently well with the composition of the derivatives of cholesterin. — Older formulæ: $C^{36}H^{30}O$ (Chevreul); $C^{74}H^{63}O^2$ (Marchand); $C^{84}H^{72}O^6$ (Schwendler & Meissner); $C^{81}H^{69}O^3$ (Zwenger); $C^{28}H^{25}O$ (Heintz).

Decompositions. 1. Cholesterin, submitted to *dry distillation*, boils, turns yellow and brown, and yields first a colourless then a reddish-yellow neutral distillate, which is a solution of cholesterin in empyreumatic oil, leaving a small quantity of charcoal (Chevreul). When rapidly distilled, it leaves merely a trace of charcoal, and yields at first nearly pure cholesterin, afterwards a mixture of cholesterin and empyreumatic oil. When it is slowly distilled, more empyreumatic oil is produced (Bussy & Lecanu, *J. Pharm.* 12, 624; *Mag. Pharm.* 17, 149).

Heintz obtained by the distillation of cholesterin (*a*) a crystalline distillate, consisting chiefly of undecomposed cholesterin; (*b*) a turpentine-like liquid, containing cholesterin, a little cholesterone, and empyreumatic oil; and (*c*) empyreumatic oil. Gases were evolved towards the end of the operation only, when carbon began to be deposited. — The empyreumatic oil may be resolved into (1) a portion boiling below 175°, smelling like coal-tar, containing equal numbers of atoms of carbon and hydrogen, permanent in the air, and lighter than water; (2) a colourless thick oil, which distils about 240°, absorbs oxygen and turns brown in the air, and contains 22 atoms of hydrogen to 28 of carbon.—If the distillation be stopped when about $\frac{1}{10}$th remains behind, and the residue be treated with ether, there remains undissolved a brown, loose powder, containing 93 81 p. c. C. and 5·46 H, corresponding to the formula C^3H. It dissolves with great difficulty in ether, is insoluble in alcohol, and is not affected by alcoholic potash. Cholesterin also breaks up, on dry distillation, into a hydrocarbon richer, and other hydrocarbons less rich, in hydrogen (Heintz).

2. The vapour of cholesterin passed through a red-hot tube yields marsh gas and olefiant gas, together with a thick brown tar (Heintz). —When kindled in the air cholesterin burns like wax.

3. Cholesterin treated with moist *bromine* (according to xvi, 316) yields a brominated product containing 35·98 p. c. of bromine, of lower melting-point and less hard than stearin (Lefort, *N. J. Pharm.* 24, 113). The formula $C^{52}H^{41}Br^3O^2$ requires 38·7 p. c. Br. (Kr.).—Dry bromine acts like chlorine, producing a yellow loose powder (Schwendler & Meissner).—4. In a current of dry *chlorine*, cholesterin becomes hot and melts, evolving hydrochloric acid and acquiring a yellow to brown colour. With less chlorine it runs into a colourless mass. In diluted chlorine in yields chlorocholesterin (Schwendler & Meissner). Lefort obtained with moist chlorine a product containing 21·30 p. c Cl. See also Reinsch (*Répert*, 77, 328).—5. *Pentachloride of phosphorus* acts violently on cholesterin, converting it into a brown, thick mass, which afterwards solidifies to crystalline chloride of cholesteryl (Planer, *Ann. Pharm.* 118, 25).

6. Cholesterin is attacked by moderately strong *nitric acid* on warming only, being converted into a brown resin, which afterwards dissolves: if the action be prolonged, acetic acid and traces of other acids are obtained as volatile products, whilst the residue contains cholesteric acid (xvi, 157) and a little soft resin (Redtenbacher, *Ann. Pharm.* 57, 167). According to Pelletier & Caventou, 1 part of cholesterin dissolved in 1 part of fuming nitric acid yields their *cholesteric acid*, which crystallises in needles melting at 58° and forms yellow and red salts. But neither Gmelin & Gugert (*Ed.* 3, 507) nor Brandes (*A. Br. Arch.* 14, 260) succeeded in obtaining this acid.—When treated with nitric acid and with ammonia, in the same manner as uric acid (x, 462) in the murexide reaction, cholesterin acquires a deep-red colour, which is not essentially altered by fixed alkalis (Schiff, *Ann. Pharm.* 101, 330).

7. Cholesterin is coloured red-brown by *phosphoric acid* at a high temperature (Schiff). When boiled with the aqueous acid it yields alpha- and a little beta-cholesterone (p. 109), with elimination of water, and when kept melted too long, a resin, probably an amorphous cholesterone, corresponding to the alpha-cholesterilin formed by the action of oil of vitriol (Zwenger).—8. In *oil of vitriol* it rapidly assumes a pomegranate-yellow colour, coheres to a pitchy mass, evolves sulphurous acid, and carbonises when heated (Chevreul). When cholesterin is added to oil if vitriol diluted with half its volume of water at 60° or 70°, and oil of vitriol is dropped into the mixture until the whole of the cholesterin is converted into a soft, dark-red mass, three solid hydrocarbons (Zwenger's cholesterilins, p. 108) are formed and may be precipitated in the form of a red mass by water. No conjugated sulphuric

acid is formed in the reaction. Undiluted oil of vitriol produces the same hydrocarbons, but speedily alters them by further action (Zwenger). When warmed with a mixture of 5 volumes of oil of vitriol and 1 volume of water on the object-holder of a microscope, cholesterin acquires a fine carmine-red colour; with 4 volumes of oil of vitriol to 1 volume of water it becomes blue, without warming; with 3 to 1 violet; with 2 to 1 pale-lilac (Moleschott, *Compt. rend.* 40, 361).—On adding *tincture of iodine* to the mixture of cholesterin with *oil of vitriol* and $\frac{1}{5}$th its volume of water, the carmine-red colour changes to violet, grey, yellowish-green, sap-green, and blue: Meckl's and Virchow's reaction.—With *sugar* and *sulphuric acid*, cholesterin acquires a brown colour (M. S. Schultz): it gives colours similar to those obtained with the bile-acids, differing according to the strength of the acid, unstable, and quickly passing into dirty olive-green (Beneke).

9. When cholesterin is evaporated with *hydrochloric acid* mixed with one-third of its volume of aqueous ferric chloride, the residue is coloured a fine red-violet, changing to blue-violet; with sulphuric instead of the hydrochloric acid, the colour is carmine-red, afterwards violet. *Chloride of gold* and *chloride of platinum* act like ferric chloride. *Bichromate of potash* and hydrochloric acid form a green solution, which leaves a violet residue (Schiff). *Nitrate of mercury* does not affect cholesterin (Schiff, *Ann. Pharm.* 115, 315).

10. Cholesterin is not saponifiable by boiling *potash-ley.* — When melted with an equal weight of caustic potash, it turns yellow and gives off a yellow oil, which is viscid and non-crystalline after cooling, and exhibits a green iridescence by reflected light (Reinsch, *Répert.* 77, 328).

11. Cholesterin heated with *hydrochloric*, *acetic*, *butyric*, *benzoic*, or *stearic acid* to 200°, or in some cases to a lower temperature, forms compounds analogous to the compound ethers.

In the case of the monobasic acids, 1 atom of cholesterin combines with 1 atom of acid, with elimination of 2 atoms of water. — The compounds are purified by removing the excess of cholesterin with boiling alcohol, in which the ethers are nearly insoluble. — They are solid, crystalline, more easily fusible than cholesterin, and neutral. They are decomposed somewhat less easily than spermaceti by heating to 100° with lime for eight or ten days, yielding cholesterin and the lime-salt of the acid. They undergo decomposition when heated, evolving an aromatic odour, giving off volatile products, and leaving a little charcoal. — Oil of vitriol colours them orange-yellow, and if after some time a little water and iodine-solution be added to the mixture, there is sometimes, but not always, produced a bluish coloration visible under the microscope, which colour is also exhibited by cholesterin when similarly treated (Berthelot).

Combinations. With Water. Hydrated Cholesterin. — Crystallises from alcohol or ether [and from nearly absolute alcohol (Heintz)] in delicate white pearly laminæ. Tabular crystals of the monoclinic system. Fig. 110 without a, but with the faces m and t of fig. 82. $u : u' = 139° 45'$; $u : t = 110° 14'$; $m : i = 100° 30'$; $m : f = 131° 34'$; $i : f = 127° 50'$; $i : u = 99° 51'$; $f : u = 128° 35'$ (Heintz). Lighter than water (Chevreul). — It loses the whole of its water over oil of vitriol (Heintz) or at 100°, and also when melted.

	Hydrated.		Pleischl.	Kühn.	Heintz.
$C^{52}H^{44}O^2$	372	95·38			
2 HO	18	4·62	5·2	5·2	4·62 to 5·72
$C^{52}H^{44}O^2$ + 2aq.	390	100·00			

Schwendler and Meissner doubted the presence of water: their cholesterin with 2·83 p. c. of water, crystallised from ether-alcohol, cannot be obtained, and was probably partially effloresced hydrated cholesterin (Heintz).

Cholesterin is insoluble in *water*.—When melted with *phosphorus*, it solidifies to a crystalline mass, and crystallises from alcohol free from phosphorus (Kühn).

Cholesterin-soda. — Rock-oil, previously purified by long standing over sodium, is saturated with dry cholesterin, and pieces of sodium are dropped into the solution, whereupon an evolution of hydrogen takes place and the sodium becomes covered with white crusts. After standing and shaking till the crusts no longer increase, the liquid is filtered, and the solid is pressed between dried blotting-paper and preserved over oil of vitriol. — From a strong solution in hot chloroform or rock-oil, it crystallises in delicate needles. Melts at 150°, and undergoes decomposition at 190°. Decomposed by water and more rapidly by weak spirit (Lindenmeyer).

			Lindenmeyer. *mean.*
52 C	212	79·19	79·20
43 H	43	10·91	11·07
2 O	16	4·06	4·89
Na	23	5·84	
$C^{52}H^{43}NaO^2$	394	100·00	100·00

Cholesterin with Acetic Acid.—Cholesterin dissolves in hot glacial acetic acid, forming a solution which deposits crystals on cooling (Beneke). The saturated solution solidifies, on cooling, to a mass of four-sided, long thin needles, which, after pressing and drying, melt at 110°, and give off 12·7 to 13·7 per cent. of acetic acid. — In alcohol the compound becomes opaque and dissolves, the solution subsequently depositing crystals of cholesterin (Hoppe-Seyler and Zalesky, *J. pr. Chem.* 90, 331). The crystals dried over lime are free from acetic acid (Beneke).

			Zalesky.
$C^{52}H^{44}O^2$	372	86·11	
$C^4H^4O^4$	60	13·89	12·7 to 13·7
$C^{52}H^{44}O^2,C^4H^4O^4$	432	100·00	

Cholesterin dissolves in *butyric* and *valerianic acids* when warmed, and in *caproic* and *caprylic acids* in the cold. The solutions deposit long prisms. It is nearly insoluble in *lactic acid* and in aqueous *oxalic* and *glycollic acids* (Beneke).

Cholesterin dissolves easily in *bisulphide of carbon* (Kühn). — It dissolves so freely in hot *wood-spirit* that the solution solidifies to a crystalline mass on cooling (Gmelin). — It is soluble in 6·65 parts of *chloroform* at 20° (Lindenmeyer). — Dissolves in 16·5 parts of absolute *alcohol* at 15°, in 4·9 parts at 34·5°, and in all proportions of the boiling liquid (Kühn). Nearly insoluble in cold aqueous alcohol; soluble in 9 parts of boiling alcohol of sp. gr. 0·84, and in 5·55 parts of sp. gr. 0·816 (Chevreul). The solution deposits most of the cholesterin on addition of water. — Cholesterin dissolves more freely in warm than in cold *ether;* according to Kühn in 12·1 parts of ether at 0°, in 3·7 parts at 15°, and in 2·2 parts boiling.

It dissolves freely in *coal-oil* (Hoppe-Seyler); slightly in boiling *oil of turpentine* (Bostock); as freely in turpentine as in ether (Kühn). *Fat oils* also dissolve cholesterin (Fourcroy & Vauquelin). — It forms a turbid liquid with *soap-water*, and swells up in microscopic myelin-like forms (Beneke). According to Strecker it dissolves in aqueous *taurocholic* and other bile-acids.

Conjugated Compounds of the Primary Nucleus $C^{52}H^{42}$.

Choride of Cholesteryl.

$$C^{52}H^{33}Cl = C^{52}H^{42},HCl,$$

BERTHELOT. *N. Ann. Chim. Phys.* 56, 61.
PLANER. *Ann. Pharm.* 118, 25.

Cholesterine chlorhydrique. Chlorcholestearyl. Cholesterinchlorafer.

1. Cholesterin is heated to 100° with strong hydrochloric acid for eight or ten hours in a sealed tube; the product is washed with water; the portion remaining undissolved is taken up with ether and shaken with weak potash-ley; and the ethereal solution is evaporated. There then remains a neutral translucent resin, which contains hydrochloric acid, but gives up a part of it on purification (Berthelot). — 2. By the action of pentachloride of phosphorus on cholesterin a brown crystalline mass is obtained, which, after pressing and boiling with water, crystallises from alcohol and ether in long needles. The crystals melt at about 100°: appear while cooling of a splendid violet colour by reflected, and yellowish-green by transmitted light; are not decomposed by boiling strong potash-ley; dissolve easily in ether and sparingly in alcohol (Planer).

	Needles.		Planer. *mean.*
52 C	312	79·89	79·78
43 H	43	11·02	11·18
Cl	35·5	9·09	8·63
$C^{52}H^{43}Cl$	390·5	100·00	99·59

Acetate of Cholesteryl.

$$C^{56}H^{46}O^{4} = C^{52}H^{43}O,C^{4}H^{3}O^{3}.$$

BERTHELOT. *N. Ann. Chim. Phys.* 56, 60.

Cholesterine acetique.

Obtained in the same way as the butyrate, and freed in like manner from excess of acid.

On heating to 100° equal numbers of atoms of cholesterin and glacial acetic acid, 17 5 p. c. is converted into ether in nine hours, and 34·1 p. c. in 40 hours (Berthelot & Péan de St. Gilles, *Compt. rend.* 55, 42).

The compound dissolves in boiling alcohol, and therefore cannot be separated from free cholesterin with certainty.—It yields acetic acid and cholesterin by saponification.

Butyrate of Cholesteryl.

$$C^{60}H^{50}O^4 = C^{52}H^{43}O,C^8H^7O^3.$$

BERTHELOT. *N. Ann. Chim. Phys.* 56, 59.

Cholesterine butyrique.

Cholesterin is heated to 200° with butyric acid for eight or ten hours in a sealed tube. The product is first treated with a strong aqueous solution of carbonate of potash: ether is then added, and the whole is shaken. The ethereal layer is decanted, filtered, decolorised with animal charcoal, and evaporated, when a mixture of free cholesterin and cholesteric butyrate remains, the former of which is removed by repeated boiling with alcohol. The undissolved butyrate may be crystallised from ether.

Neutral colourless crystals, which are easily fusible, and afterwards remain semi-soft and translucent till the mass is nearly cold.

			Berthelot.
60 C	360	81·45	81·9
50 H	50	11·31	11·3
4 O	32	7·24	6·8
$C^{52}H^{43}O,C^8H^7O^3$	442	100·00	100·0

When melted on platinum-foil, it evolves an odour of spice and butyric acid, takes fire, and burns with a red smoky flame.—When submitted to *dry distillation*, it yields acid products.—It is resolved by *alkalis* into cholesterin and butyric acid.

It is nearly insoluble in cold *alcohol*, but dissolves rather more freely than stearate of cholesteryl in boiling alcohol, and very easily in *ether*.

Benzoate of Cholesteryl.

$$C^{66}H^{48}O^4 = C^{52}H^{43}O,C^{14}H^5O^3.$$

BERTHELOT. *N. Ann. Chim. Phys.* 56, 61.

Cholestérine benzoique.

Cholesterin is heated to 200° with benzoic acid for 8 or 10 hours, and the contents of the tube, intimately mixed with aqueous carbonate of potash by trituration, are shaken with ether (with addition of a little caustic potash, if necessary) till a test-portion of the ether no longer gives up acid to water. The ether is then decanted, filtered, decolorised with animal charcoal, and evaporated. The residue is freed from uncombined cholesterin by boiling it repeatedly with alcohol, and the benzoate is crystallised from ether.

Shining white laminæ, appearing rectangular and thicker than cholesterin under the microscope. Melts at 125° to 130°. Neutral. When carefully heated in small quantity it volatilises without decomposing.

			Berthelot.
66 C	396	83·19	82·6
48 H	48	10·09	10·4
4 O	32	6·72	7·0
$C^{52}H^{43}O,C^{14}H^{5}O^{3}$	476	100·00	100·0

Decompositions. Heated above its melting-point on platinum foil, it evolves a peculiar aromatic odour and *burns* with smoky flame.— Submitted to *dry distillation* in larger quantity, it yields a sublimate of benzoic acid.— It is very slowly resolved into cholesterin and benzoic acid by slaked lime at 100°.

Dissolves very slightly in *alcohol*, even when boiling, but easily in *ether*.

Stearate of Cholesteryl.

$C^{88}H^{78}O^{4} = C^{52}H^{43}O,C^{36}H^{35}O^{3}$.

BERTHELOT. *N. Ann. Chim. Phys.* 56, 57.

Cholestérine stearique.— Obtained from cholesterin and stearic acid in the same manner as stearate of cetyl (xvi, 128).

White shining needles. Neutral. Melts at about 65° to a transparent liquid, which solidifies to a dead-white amorphous mass.

	Needles.		Berthelot.
88 C	528	82·76	82·9
78 H	78·	12·22	12·1
4 O	32	5·02	5·0
$C^{52}H^{43}O,C^{36}H^{35}O^{3}$	638	100·00	100·0

Decompositions. Stearate of cholesteryl *heated* on platinum foil evolves aromatic, somewhat agreeably smelling vapours, which burn with a white flame.—By dry distillation it yields an acid product, and leaves no charcoal.— It is resolved into cholesterin and stearate of lime by heating to 100° with slaked lime, the decomposition being completed only in 8 or 10 days.

It is nearly insoluble in *alcohol* either cold or boiling, but easily soluble in cold *ether*.

Appendix to Cholesterin.

1. Ambrein.

BUCHHOLZ. *N. Tr.* 18, 1, 28.
JOHN. *Berl. Jahrb.* 1818, 104.
PELLETIER & CAVENTOU. *J. Pharm.* 6, 50; *N. Tr.* 4, 2, 333.
PELLETIER. *Ann. Chim. Phys.* 51, 188; *Schw.* 67, 84; *Ann. Pharm.* 6, 24.

Amberharz (John). *Amberstoff* (Buchholz). *Amberfett.* — Discovered by Buchholz. — The chief constituent of grey ambergris. The excrement of *Delphinus globiceps* contains a substance which resembles ambrein, but has a higher melting-point (Chevallier & Lassaigne, *J. Pharm.* 7, 279).

Ambergris is boiled with alcohol, and the liquid is filtered, whereupon the ambrein crystallises, and may be purified by pressing and recrystallisation.

White, delicate needles, arranged in tufts. Softens at 25°, and melts at 30° (Pelletier & Caventou). Melts at 36° (Pelletier), at 37·5° (John). Tasteless and inodorous when free from volatile oil; after repeated melting it smells like resin.

According to Pelletier and Caventou, it contains 82·2 p. c. C., 13·3 H., and 4·5 O., from which numbers Berthelot calculates the formula $C^{50}H^{48}O^2$ (*N. Ann. Chim. Phys.* 56, 67).

Ambrein heated in a retort turns brown, evolves white vapours, and distils almost entirely unchanged (Pelletier & Caventou). — When heated on platinum foil, it is almost completely volatilised in white fumes (Buchholz). — It turns soft in strong nitric acid, and when heated therewith dissolves, and is converted into ambreic acid, with evolution of nitric oxide (Pelletier & Caventou).

To prepare *ambreic acid*, the solution of ambrein in nitric acid is evaporated to dryness; the residue is washed with cold water; boiled with water and a little carbonate of lead; again washed with water so long as it gives up nitrate of lead; dissolved in boiling alcohol, and filtered. — The acid crystallises in small yellowish-white tables, which redden litmus, and do not melt at 100°. — It dissolves to a very slight extent in water, and is partially deposited from its solution in boiling water as it cools. The neutral potash-salt is easily soluble; the acid salt is precipitated in flocks from an alcoholic solution of the acid by the addition of a little potash. The neutral salt gives dark-yellow precipitates with metallic salts. Ambreic acid dissolves easily in alcohol, less freely in ether (Pelletier & Caventou).

Ambrein is not saponified by boiling for eight hours with strong potash-ley.

It dissolves freely in absolute *alcohol* and does not crystallise on cooling or evaporation (John). The solution in warm weak spirit yields a large quantity of crystals on cooling (Pelletier). — It is easily soluble in *ether*, and in *volatile* and *fixed oils* (Buchholz).

2. Castorin.

Bizio. *Brugn. Giorn.* 17, 174; abstr. *N. Tr.* 11, 1, 300.
Brandes. *Br. Arch.* 16, 281.
Winckler. *Mag. Pharm.* 13, 171.

Castoreum camphor. — Observed by Fourcroy, Barneveld, and Bohn. — Occurs in castoreum, which contains also cholesterin (Brandes, Lehmann), a resin insoluble in ether, and Brandes' *castoreum resinoïd* (*N. Br. Arch.* 1, 183).

Preparation. Castoreum is boiled with 6 parts of alcohol of sp. gr. 0·85, and the solution is filtered and evaporated to one-half. The crystals of castorin thus obtained are washed first with cold alcohol, then with aqueous ammonia or potash, dissolved in alcohol, and decolorised with animal charcoal (Bizio). The alcoholic decoction of castoreum deposits fat on cooling, which may be separated by filtration (Brandes).

Properties. — Castorin crystallises in granules or in tufts of white transparent needles, very light and very friable (Bizio). It melts in boiling water to an oil, which floats on the surface and solidifies to a transparent mass. When boiled with water it volatilises to some extent with the aqueous vapour, so that the distillate turns cloudy after some time (Brandes). It has a faint odour of castoreum and a peculiar taste. Neutral (Bizio).

Decompositions. Castorin yields by dry distillation a pomegranate-yellow oil, which solidifies to a soft resin. — It takes fire, and burns with a bright flame, leaving charcoal. — It is decomposed by prolonged boiling with nitric acid, the decoction yielding on evaporation yellow needles and granules of Brandes' *castoric acid.* — The easily formed solution of castorin in oil of vitriol is perfectly colourless (Brandes); it is of a yellowish-green colour, precipitable by water, and when heated evolves sulphurous acid, with separation of charcoal (Bizio).

Castorin is insoluble in cold, and very slightly soluble in boiling *water*, from which it crystallises in a few days (Bizio). — It is soluble, according to Brandes, insoluble according to Bizio, in warm dilute *sulphuric acid;* freely soluble in hot strong *nitric acid* (Bizio), from which it is precipitated by water (Winckler). — According to Bizio, it is insoluble in hot aqueous ammonia, potash, and soda; but according to Brandes it dissolves freely in hot strong potash-ley, and is deposited on cooling, or on the addition of water.

Castorin is nearly insoluble in cold, but freely soluble in boiling *acetic acid.* The solution deposits most of the castorin in needles, after some weeks only, and when allowed to evaporate spontaneously leaves it in crystals (Brandes). — It is but little soluble in cold, and slowly soluble in boiling *alcohol* (Bizio). It dissolves in 120 parts of boiling 75 p. c. alcohol, forming a solution which coagulates completely in the cold; it is more freely soluble in absolute alcohol (Brandes). — It dissolves easily in *ether*, slightly in cold, and freely in hot *oil of turpentine*, and in hot *olive oil* (Brandes).

3. Agaricin.

The edible mushroom contains a non-saponifiable buttery fat, which melts at 35°, and contains 56·62 p. c. C., 10·84 H., 31·95 O., and 0·59 N. (Lefort, *Comt. rend.* 42, 91). — Gobley's agaricin is obtained by exhausting dry mushroom-powder with ether, and purifying the ethereal extract by dissolving it in boiling alcohol and crystallising. It forms small white laminæ, melting at 148° to 150°, and solidifying again at 139°. It is inodorous and tasteless, contains 78·40 p. c. C., 11·10 H., and 10·50 O. Not saponifiable. Dissolves slightly in cold and in boiling alcohol, and very easily in ether (Gobley, *N. J. Pharm.* 29, 81; *Kopp's Jahresber.* 1856, 685).

4. Reichenbach's Cholesterin from Animal Tar.

Reichenbach. *Schw.* 62, 273.

Occurs in the tar obtained by the dry distillation of horse-bones, flesh, and similar bodies; not in wood or coal-tar.

The tar is submitted to repeated fractional distillation; the first third of the fluid distillate is separated; and the remainder is mixed with 3 to 6 times its volume of alcohol of sp. gr. 0·82, which precipitates eupione and paraffin; after separating these bodies, the alcoholic solution is exposed to cold, and the yellow crystals then formed are pressed and recrystallised.

Colourless needles, translucent at the edges, fatty to the touch, very brittle, of sp. gr. 0·9256. Melts at 100°, boils at 350°, and distils mostly unaltered. Solidifies to a crystalline mass on cooling. — Burns with flame. Converted by the action of chlorine into a greenish-yellow liquid. Not altered by *oil of vitriol* at first, but dissolved at a gentle heat to a colourless liquid, which solidifies to a stiff jelly on cooling, and is precipitated by water. — Not decomposed by hot strong nitric acid, in which it is only slightly soluble. — Insoluble in boiling potash-ley. — Insoluble in water, but soluble in all proportions of boiling alcohol; very easily soluble in ether, in bisulphide of carbon, and in volatile and fixed oils.

Chlorine-nucleus $C^{52}Cl^7H^{35}$.

Chlorocholesterin.

$$C^{52}Cl^7H^{37}O^2 = C^{52}Cl^7H^{35},H^2O^2.$$

Schwendler & Meissner. *Ann. Pharm.* 59, 110.

Fused and powdered cholesterin is spread in a thin layer on the bottom of a capacious flask, into which a small quantity of dry chlorine is passed, the flask being kept cold. On standing awhile the colour of the chlorine disappears, whereupon a fresh portion of the gas is admitted. After this process has been continued for some days, the mass is again powdered and then left for some time in contact with undiluted chlorine; the hydrochloric acid and excess of chlorine are expelled by a current of dry air, and the product is preserved over caustic potash.

White, loose, inodorous and tasteless powder, which cakes together between the fingers like resin and melts at 60° to a yellow liquid which solidifies in an amorphous mass.

	Dried over caustic potash.		Schwendler & Meissner. *mean.*
52 C	312	50·85	49·50
7 Cl	248·5	40·51	41·21
37 H	37	6·03	5·96
2 O	16	2·61	3·33
$C^{52}Cl^{7}H^{37}O^{2}$	613·5	100·00	100·00

According to Schwendler & Meissner, $C^{84}Cl^{12}H^{60}O^{3}$.

Chlorocholesterin evolves a little hydrochloric acid gas when long *kept*. It undergoes decomposition at a few degrees above its melting-point, and is converted into a brown porous mass, with evolution of a large quantity of hydrochloric acid. — It is not affected by alcoholic *ammonia* or *potash* in the cold, but rapidly turns brown on warming.

It is not wetted or affected by *water*. — It does not dissolve in cold 78 p.c.-*alcohol*, but runs together when warmed therewith, and melts to a mass resembling yolk of egg. Its solution in cold absolute alcohol (in which it dissolves with difficulty) deposits white amorphous granules on spontaneous evaporation. Warm *ether* dissolves it easily, but yields no crystals on evaporation.

Primary Nucleus $C^{52}H^{52}$; *Oxygen-nucleus* $C^{52}H^{44}O^{8}$.

Koussin.

? $C^{52}H^{44}O^{10} = C^{52}H^{44}O^{8},O^{2}$.

WITTSTEIN. *Repert.* 71, 25.

PAVESI. *Giornale Pharm. de Torino*; abstr. *Pharm. Viertelj.* 8, 505; *Kopp's Jahresber.* 1859, 585.

BEDALL. *Pharm. Viertelj.* 8, 505; *N. Jahrb. Pharm.* 12, 372; *Kopp's Jahresber.* 1859, 585. — *Pharm. Viertelj.* 11, 207; *N. Jahrb. Pharm.* 18, 68; *Chem. Centr.* 1863, 124; *Kopp's Jahresber.* 1862, 513.

Acrid bitter resin of Brayera anthelmintica (Wittstein). — Occurs in commercial kusso or kousso, the dried flowers of the above-named plant, which have been examined also by Viale and Latini (*Kopp's Jahresber.* 1852, 678), and contain their *hagenic acid;* by St. Martin, who found a nitrogenous *kosein;* and by Willing (*N. Repert.* 4, 51). For a summary of these investigations, see *Pharm. Viertelj.* 8, 505. — See further Martius (*N. Repert.* 3, 177); Harms (*N. Br. Arch.* 89, 301), A. Vée (*Repert. Chim. appliquée*, 1, 173; *Kopp's Jahresber.* 1859, 585).

Preparation. Coarsely-powdered kousso is macerated three times with alcohol, with addition of lime, then pressed and treated with water. The filtered extracts are mixed, freed from alcohol by distillation, filtered after cooling, and precipitated with acetic acid. The washed precipitate is dried on glass plates at the ordinary temperature (Bedall).

Properties. White or yellowish powder, appearing crystalline under the microscope. Inodorous; tastes acrid and bitter. Has an acid reaction. Free from nitrogen. Acts as a vermifuge (Bedall).

Calculation according to Bedall.			Bedall. *mean at* 125°.
52 C	312	71·56	71·19
44 H	44	10·09	10·15
10 O	80	18·35	18·66
$C^{52}H^{44}O^{10}$	436	100·00	100·00

Contains also 0·19 p. c. of ash. Bedall's formula is half the above.

Decompositions. Koussin turns brown at 150° and melts at 194°, with partial decomposition, and without volatilising. — It dissolves in *oil of vitriol*, forming a yellow solution, from which water throws down white flocks. No sugar is formed thereby, as Bedall formerly believed. — It does not reduce *alkaline solution of cupric oxide* (Bedall).

It dissolves slightly in *water*, and easily in aqueous alkalis. — The alcoholic solution is precipitated white, but incompletely, by alcoholic neutral acetate of lead. Bedall obtained lead-salts with 43·62, 66·07, and 83·11 p. c. of oxide of lead.

Koussin is soluble in all proportions of strong *alcohol* and *ether*, but only sparingly soluble in weak spirit, from which it is deposited in the form of a white resin on cooling (Bedall).

Primary Nucleus $C^{52}H^{58}$; *Oxygen-nucleus* $C^{52}H^{44}O^{14}$.

Paris Resin.

$$C^{52}H^{44}O^{16} = C^{52}H^{44}O^{14},O^{2}.$$

WALZ. *N. Jahrb. Pharm.* 13, 361.

Extracted by ether from crude paridin (p. 125), together with leaf-green, and purified by evaporating the ether, dissolving the residue in alcohol, digesting with animal charcoal, and precipitating the filtrate with water.

Soft, easily fusible mass, smelling of the plant from which it is derived.

			Walz.	
52 C	312	64·46	66·23	64·36
44 H	44	9·09	8·94	9·11
16 O	128	26·45	24·83	26·53
$C^{52}H^{44}O^{10}$	484	100·00	100·00	100·00

According to Walz, it differs from paridol in containing two atoms of water less.

It colours *oil of vitriol* dark-brown. — Dissolves in fuming *nitric acid* with brown colour; slightly in *hydrochloric acid*, from which it is precipitated by water; easily in aqueous *ammonia* and *potash*, precipitable by acids. — Easily soluble in *ether*.

Paridol.

$$C^{52}H^{46}O^{18} = C^{52}H^{44}O^{14},O^{2},2HO.$$

Walz. *N. Jahrb. Pharm.* 13, 359.

Formation. Paridin breaks up, on boiling with dilute sulphuric acid, into paridol and sugar. — There is formed at the same time amorphous paridin, which Walz formerly regarded as a third decomposition product:

$$C^{64}H^{56}O^{28} + 2HO = C^{52}H^{46}O^{18} + C^{12}H^{12}O^{12}.$$

Preparation. Paridin is boiled with 3 parts of oil of vitriol and water for a few hours, or until the finely divided paridin is converted into an oil; the paridol is dissolved in ether, and the ethereal solution left to evaporate.

Soft fusible mass, having a fatty odour.

			Walz.	
52 C	312	62·16	61·04	61·62
46 H	46	9·16	9·19	9·29
18 O	144	28·68	29·77	29·09
$C^{52}H^{46}O^{18}$	502	100·00	100·00	100·00

Paridol dissolves in *oil of vitriol* with fine red colour, changing to brown. — It dissolves in fuming *nitric acid*, forming a solution, which deposits a yellow body on standing. — It is insoluble in aqueous *ammonia* or *potash*, but easily soluble in *ether*.

Glucosides of Paridol.

1. Paridin.

G. F. Walz. *Jahrb. pr. Pharm.* 4, 3; 5, 284; 6, 10. — *N. Jahrb. Pharm.* 13, 174, and 355; *Kopp's Jahresber.* 1860, 543.
Delffs. *N. Jahrb. Pharm.* 9, 25; *Chem. Centr.* 1858, 209; *N. Br. Arch.* 95, 330; *Kopp's Jahresber.* 1858, 527.

Occurs in *Paris quadrifolia*, and according to Walz, is also produced by boiling paristyphnin with acids, which, however, decompose the paridin.

Preparation. The coarsely powdered dried plant is twice exhausted with warm water, containing 2 per cent. of acetic acid, and pressed; the residue is exhausted with alcohol of sp. gr. 0·85; the extracts are distilled till the residue solidifies to a jelly, which crystallises on cooling; and the crystals are purified by recrystallisation from alcohol, with the aid of animal charcoal (Walz).

Properties. White, silky needles, tasteless at first in the dry state, but afterwards persistently acrid, not bitter. Neutral. Air-dried paridin loses 7·97 p. c. of water, at 100° (Gmelin); 9·9 to 10·4 p. c. (Delffs); that dried at 25° loses 6·92 p. c. at 100° (Walz).

Calculation according to Delffs.			Gmelin. *mean.*	Walz.	Delffs. *mean.*
32 C	192	57·83	55·49	55·07	57·68
28 H	28	8·43	7·56	7·82	8·51
14 O	112	33·74	36·95	37·11	33·81
$C^{32}H^{28}O^{14}$	332	100·00	100·00	100·00	100·00

Gmelin analysed impure paridin prepared by Walz.

According to Walz, paridin melts when *heated* to a liquid of dark blue colour, which, however, was not observed by Delffs in the purified substance. — It is decomposed by hot *oil of vitriol*, and by hot aqueous *alkalis*. — It dissolves in nitric acid of sp. gr. 1·54, forming a yellow solution, which is not precipitated by water. — When boiled with *dilute sulphuric acid*, it breaks up into paridol and sugar. 100 parts of paridin yield 75 parts of paridol and 26·2 parts of sugar (Walz).

Paridin does not dissolve in *water*, but causes it to froth like soap (Walz). Elsewhere Walz describes paridin as soluble in water, and crystallisable therefrom. — It is soluble in 50 parts of 94 p. c. *alcohol*, but nearly insoluble in *ether* (Walz).

2. Paristyphnin.

Walz. *N. Jahrb. Pharm.* 13, 355.

The bitter principle of *Paris quadrifolia*, precipitated by tannic acid.

Preparation. The mother-liquor obtained in the preparation of paridin (from which no more paridin is deposited even after driving off the whole of the alcohol), is neutralised with ammonia and precipitated with aqueous tannic acid; and the resinous precipitate, which is completely thrown down only after some days, is washed with water, dissolved in alcohol, and treated with oxide of lead. After the tannic acid is precipitated, the filtrate is freed from lead by hydrosulphuric acid, from alcohol by distillation, and evaporated to dryness. The residue is a mixture of paristyphnin, fat, and paridin, the last of which may be separated by dissolving the residue in cold water and evaporating, the paridin then crystallising. The solution is evaporated to dryness, and the residue, freed from fat by ether, is dissolved in alcohol, decolorised with animal charcoal, and allowed to evaporate spontaneously.

Properties. Yellowish-white powder, having a nauseous, bitter, acrid taste. The dust excites sneezing. Permanent in the air.

	Dried.		Walz.	
76 C	456	56·44	55·75	57·69
64 H	64	7·92	7·88	8·04
36 O	288	35·64	36·37	34·27
$C^{76}H^{64}O^{36}$	808	100·00	100·00	100·00

Decompositions. Paristyphnin boiled with dilute *sulphuric acid*, breaks up into paridin and sugar:

$$C^{76}H^{64}O^{36} + 4HO = C^{64}H^{56}O^{28} + C^{12}H^{12}O^{12}.$$

100 parts of paristyphnin, boiled with 100 parts of oil of vitriol and water, gave 80·4 parts of paridin and 24·8 parts of sugar, together with traces of paridol, formed by the further decomposition of the paridin. — It dissolves in *oil of vitriol*, forming a yellow solution, from which it is precipitated by water; and in like manner in fuming *nitric acid.*

Paristyphnin dissolves easily in *water.* It dissolves slowly in aqueous *ammonia*, without coloration; and in potash-ley of sp. gr. 1·23, with yellow colour. It is easily soluble in *alcohol*, but insoluble in *ether.*

Appendix to Compounds containing 52 atoms of Carbon.

Helleboreïn.

$$C^{52}H^{44}O^{30} = C^{28}H^{20}O^{6},2C^{12}H^{12}O^{12}.$$

Aug. Husemann & Marmé. *Ann. Pharm.* 135, 55; *Krit. Zeitschr.* 8, 501; *Chem. Centr.* 1865, 681; *N. Repert.* 14, 230; *Schweiz. Pharm. Wochenschr.* 1865, 2.

A glucoside from the roots of *Helleborus niger* and *H. viridis.* — Vauquelin (*Berl. Jahrb.* 1808, 1) obtained from the roots of *Helleborus hiemalis* an *acrid soft resin.* Feneulle & Capron (*J. Pharm.* 7, 503) and Riegel (*N. Br. Arch.* 24, 33) examined the root of *Helleborus niger* without arriving at any particular result.

Scattergood's statement (*N. Br. Arch.* 46, 128) that *Helleborus viridis* contains veratrin and a resinous modification thereof requires confirmation, to show that he has not confounded helleborin with veratrin.

Preparation. From the root of *Helleborus niger*, which contains more helleboreïn than that of *H. viridis.* A decoction of the comminuted root is precipitated with basic acetate of lead, not in excess; and the filtrate freed from dissolved lead by means of sulphate of soda is concentrated and precipitated with tannic acid. The precipitate thus formed is pressed, agitated with water, and again pressed. It is then triturated to a thin pulp with alcohol, mixed with oxide of lead, and dried, so much oxide of lead being employed that a test-portion of the dry mass shall not yield to alcohol any substance that gives a coloration with ferric chloride. The dry mass is boiled with alcohol; the alcoholic liquid is concentrated and mixed with ether; and the resinous flocks thereby thrown down are dried over oil of vitriol. The product is purified by redissolving it in alcohol and precipitating with ether.

Properties. Helleboreïn crystallises from very strong alcoholic solutions, when left at rest, in transparent warts consisting of needles, which rapidly become chalk-white in the air. Aqueous solutions leave a yellowish transparent resin on evaporation. Very hygroscopic. Tastes sweetish. Poisonous to animals. — The aqueous solution reddens litmus very faintly.

	Dried at 120°.		Husemann & Marmé. *mean.*
52 C	312	52·35	52·27
44 H	44	7·38	7·09
30 O	240	40·27	40·64
$C^{52}H^{44}O^{30}$	596	100·00	100 00

Helleboreïn acquires a straw-yellow colour and cakes together when *heated* above 160°; at 230° it turns pasty and brown; and at 290° melts to a viscid liquid and carbonises. — It dissolves in *oil of vitriol* with brown-red colour, changing to violet. — It is not altered by boiling with *potash-ley*, or by *baryta-water* at 140°, but quickly breaks up on boiling with *dilute acids* into 59·85 per cent. of sugar and 40 per cent. of helleboretin, which separates in blue flocks:

$$C^{52}H^{44}O^{30} = C^{28}H^{20}O^{6} + 2C^{12}H^{12}O^{12}.$$

(calc. 60·40 p. c. of sugar and 39·60 of helleboretin).

Helleboreïn is very easily soluble in *water*, less freely in *alcohol*, and insoluble in *ether*.

Appendix to Helleboreïn.

1. *Helleboretin.* — The fine dark blue flocks deposited on boiling helleboreïn with acids, form, after washing and drying, a grey-green amorphous powder. Inodorous and tasteless. Not poisonous. Melts above 200° to a dark brown-red liquid and carbonises. Dissolves in oil of vitriol, forming a brownish-red solution, which is precipitated by water. — It is insoluble in water and ether, but easily soluble in alcohol, with violet colour (Husemann & Marmé).

			Husemann & Marmé. *mean.*
28 C	168	71·19	71·20
20 H	20	8·47	8·48
6 O	48	20·34	20·32
$C^{28}H^{20}O^{6}$	236	100·00	100·00

2. Helleborin.

W. Bastick. *Pharm. Journ. Trans.* 12, 74; *Pharm. Viertelj.* 2, 388; *N. Repert.* 2, 61; *N. J. Pharm.* 23, 205, and 24, 159; *Kopp's Jahresber.* 1853, 482.
Husemann & Marmé. *Ann. Pharm.* 135, 61.

Discovered by Bastick in black hellebore root. — Occurs in traces in black, but more abundantly in green hellebore root, especially in old thick roots, of which 25 pounds yield 4 or 5 grammes (Husemann & Marmé).

Preparation. The comminuted root is boiled repeatedly with alcohol, and the decoctions are evaporated to a small bulk. The residue containing helleborin, helleboreïn, and a large quantity of green fat is shaken repeatedly with boiling water, which takes up the first two constituents and deposits the helleborin in crystals on evaporation. It is purified by recrystallisation from boiling alcohol (Husemann & Marmé). Bastick exhausts the root with acidified alcohol, distils, supersaturates the residue with carbonate of soda, and extracts the helleborin with ether.

Properties. Shining white needles, which do not melt at 250°. Tasteless in the dry state, but very acrid and burning in alcoholic solution. Powerfully narcotic (Husemann & Marmé). Without action on vegetable colours (Bastick).

	Crystals.		Husemann & Marmé. *mean.*
72 C	432	75 78	75·53
42 H	42	7·37	7·51
12 O	96	16·85	16·96
$C^{72}H^{42}O^{12}$	570	100·00	100 00

Bastick supposes the body to contain nitrogen.

Helleborin melts above 250° and then carbonises. — Oil of vitriol poured upon it turns it bright-red and dissolves it; water added to the solution throws down most of the helleborin in white flocks. — It breaks up into sugar and helleboresin, with assimilation of 8 atoms of water when boiled with *dilute sulphuric acid*, or more completely when heated with solution of zinc chloride:

$C^{72}H^{42}O^{12} + 8HO = C^{60}H^{38}O^{8} + C^{12}H^{12}O^{12}$ (Husemann & Marmé). — When heated with *nitric acid* it yields oxalic acid (Bastick).

Helleborin is insoluble in cold *water*. It is not altered by *dilute acids* and *alkalis*, and does not combine with them. It is not precipitated by *iodide of potassium*, *neutral acetate of lead*, or *mercuric chloride* (Bastick).

Helleborin dissolves easily in *alcohol* and in *chloroform;* sparingly in *ether* and *fat oils* (Husemann & Marmé).

3. *Helleboresin.* — Obtained by boiling helleborin with solution of zinc chloride (which, on account of its high boiling-point, acts more powerfully than dilute sulphuric acid) as a brown resin containing zinc, which is powdered, boiled with hydrochloric acid, dissolved in boiling alcohol, and precipitated with water. — White flocks drying to a greyish white powder. Softens at 140°—150°, at the same time turning brown. Tasteless. — Insoluble in water; slightly soluble in ether; easily soluble in alcohol (Husemann & Marmé).

			Husemann & Marmé.
60 C	360	77 92	78·02
38 H	38	8·22	7·86
8 O	64	13 86	14·12
$C^{60}H^{38}O^{8}$	462	100·00	100·00

COMPOUNDS CONTAINING 54 ATOMS OF CARBON.

Primary Nucleus $C^{54}H^{48}$; *Oxygen-nucleus* $C^{54}H^{44}O^4$.

Chenocholic Acid.

$$C^{54}H^{44}O^8 = C^{54}H^{44}O^4,O^4.$$

HEINTZ & WISLICENUS. *Pogg.* 108, 547; *J. pr. Chem.* 78, 190; *Chem. Centr.* 1859, 873; *Rép. Chim. pure* 2, 106; *Kopp's Jahresber*, 1859, 634.
OTTO. *Ann Pharm.* 149, 198.

Chenocholalic acid.

Produced, together with taurine, by boiling taurochenocholic acid with alkalis or baryta-water. — An aqueous solution of taurochenocholic acid is boiled with a large excess of hydrate of baryta for 36 hours, or until the originally dense precipitate becomes granular. The liquid is then allowed to cool, and the insoluble baryta-salt is washed and decomposed with hydrochloric acid. The chenocholic acid thus liberated is purified by washing, pressing, dissolving it in alcohol, and evaporating. If it still contains nitrogen, derived from undecomposed taurochenocholic acid, it is again treated with baryta-water, or boiled for 6 hours with potash-ley, when the potash-salt, which is insoluble in the excess of potash-ley, is deposited on cooling. It is decomposed in the same manner as the baryta-salt.

Properties. Pale-yellow resin, obtained on one occasion in indistinct crystals from a solution in weak alcohol after long standing. After drying at 100° it is triturable to a highly electric powder. Has an acid reaction.

Dried at 100°.			Heintz & Wislicenus. *mean.*	Otto.
54 C	324	75·00	75 31	75·1
44 H	44	10·19	10·08	10·1
8 O	64	14·81	14·61	14·8
$C^{54}H^{44}O^8$	432	100·00	100 00	100 0

Heintz and Wislicenus adopt the above in preference to the equally possible formula $C^{54}H^{42}O^8$. — Homologous with hyocholic acid.

Chenocholic acid produces with *sugar* and *oil of vitriol* the blood-red coloration of the bile-acids (p. 66).

It is insoluble in *water*. — Does not dissolve in cold strong *potash-ley*, but combines with the base, especially on warming, to form a salt which dissolves in water and is deposited from its solution in absolute alcohol as an amorphous mass on evaporation, and thrown down from the same solution by ether in the form of a tough transparent precipitate. This potash-salt precipitates flocks soluble in alcohol from many metallic salts and from neutral acetate of lead.

Chenocholate of Baryta. — The flocks obtained by double decomposition are precipitated by ether from their solution in absolute alcohol in small white glassy needles. — Dissolves with great difficulty in water, but more easily in alcohol, forming solutions from which carbonic acid throws down carbonate of baryta.

			Heintz & Wislicenus.	
	Dried at 100°.		*mean.*	Otto.
54 C	324	64·86	64·70	65·1
43 H	43	8·61	8·45	8·5
7 O	56	11·21	11·46	10·9
BaO	76·5	15·32	15·39	15·5
$C^{54}H^{43}BaO^8$	499·5	100·00	100·00	100·0

The acid dissolves in *alcohol* and *ether*.

Taurochenocholic Acid.

$$C^{58}NH^{49}S^2O^{12} = C^4NH^6S^2O^5,C^{54}H^{43}O^7.$$

TH. MARSSON. *N. Br. Arch.* 58, 138.
HEINTZ & WISLICENUS. *Pogg.* 108, 547.
OTTO. *Ann. Pharm.* 149, 185; *Kopp's Jahresb.* 1868, 823.

Chenocholic acid. Discovered by Marsson in goose-bile.

Preparation of the Soda-salt. Goose-bile is freed from the greater part of its mucus by the addition of a large quantity of alcohol; the filtrate is evaporated; the dry residue is treated with absolute alcohol; and the solution, filtered from mucus and colouring matter, is mixed with ether, which retains in solution fat and a peculiar crystalline substance, whilst salts of taurochenocholic acid are thrown down as a plaster-like precipitate. This precipitate contains potash, which is removed by precipitating its concentrated aqueous solution with Glauber's salt. The viscid drops thus thrown down are collected after some days, when they have become almost hard, purified by again dissolving and precipitating them as before, then dried, dissolved in [90 per cent. (Marsson)] alcohol, and mixed with ether. The precipitated soda-salt still contains a small quantity of an acid precipitable by neutral acetate of lead (Heintz & Wislicenus). A similar process is adopted by Marsson. — Otto finds that the soda-salt prepared as above contains small quantities of ammonia-salts. It may be obtained quite pure by precipitating with ammonia and basic lead acetate, decomposing the precipitated lead-salt with sulphuretted hydrogen, and neutralising with soda.

To prepare the acid, an aqueous solution of the soda-salt is precipitated with basic acetate of lead; the plaster-like precipitate is decomposed under alcohol by hydrosulphuric acid; and the filtrate is evaporated, when the acid remains in the form of a brown soft mass. It has an acid reaction, and when dissolved in water leaves a small quantity of white pearly crystals, probably of an acid corresponding to paraglycocholic acid (p. 61) (Heintz & Wislicenus). — This substance may be obtained in somewhat larger quantity by leaving an alcoholic solution of taurochenocholic acid in contact with ether and a little hydrochloric acid (Otto).

Inasmuch as taurochenocholic acid, when decomposed by baryta or alkalis, breaks up into chenocholic acid and taurine, probably taking up 2 atoms of water, its formula is assumed to be $C^{58}NH^{49}S^{2}O^{12}$. The composition of the soda-salt, however, agrees approximately with this formula, only when the salt is supposed to retain two atoms of water after drying at 110° (Heintz & Wislicenus). See below.

The soda salt gives the colour-reaction of the bile-acids with sugar and oil of vitriol. — Its aqueous solution is not precipitated by acetic, oxalic, or tartaric acid, but excess of hydrochloric acid throws down flocks of taurochenocholic acid, which dissolve in pure water.

Potash-salt. An alcoholic solution of goose-bile, mixed with ether, deposits on standing, tables of the soda-salt, and long thin white needles, probably of taurochenocholate of potash (Heintz & Wislicenus).

Soda-salt. Small rhombic tables, which deliquesce rapidly in the air. — Precipitated by ether from a solution of goose-bile in absolute alcohol, in the form of a plaster, which becomes crystalline only on addition of water (Marsson). It swells up in water like gum, and then dissolves completely.

	at 100—110°.		Marsson.	Heintz & Wislicenus. *mean.*	Otto. *mean.*
58 C	348	60·10	57·19	59·72	60·2
N	14	2·42	3 48	3·96	2·9
50 H	50	8·64	8·39	8·74	8·7
2 S	32	5·53	6·34	5·74	
13 O	104	17 96	19·82	16·29	
NaO	31	5·35	4·78	5·55	5·3
$C^{58}NH^{48}NaS^{2}O^{12}$ + 2aq.	579	100·00	100·00	100·00	

	at 140°.		Otto.
58 C	348	62·03	61·9 to 62·4
N	14	2·50	2·6
48 H	48	8·56	8·4 to 8·5
2 S	32	5·70	
11 O	88	15·69	
NaO	31	5·52	5.8
$C^{58}NH^{48}NaS^{2}O^{12}$	561	100·00	

Heintz & Wislicenus did not directly prove the presence of water in their salt. They supposed that it still contained taurochenocholate of ammonia, and consequently too much nitrogen. Marsson's salt contained also small quantities of phosphoric acid and chlorine. — Otto has shown that the salt dried at 110° gives off 2 at. water at 140°, and consequently that the formula of taurochenocholic acid is $C^{58}NH^{49}S^{2}O^{12}$ agreeing with its resolution by alkalis into chenocholic acid and taurine.

An aqueous solution of the soda-salt produces with *chloride of barium* and *chloride of calcium*, white flocks soluble in alcohol (Heintz & Wislicenus). The precipitates cohere in plaster-like masses on agitation. The baryta-salt dissolves on boiling, after addition of ammonia, and re-appears as the solution cools (Marsson). Sulphate of magnesia throws down from the soda-salt, after addition of ammonia flocks soluble in sal-ammoniac. *Neutral acetate of lead* produces no precipitate, but the basic acetate throws down a plaster-like precipitate which is insoluble in excess of the precipitant, and also on boiling (Marsson), but slightly soluble in alcohol (Heintz & Wislicenus). The soda-salt is precipitated also by *ferric chloride*, *salts of manganese*, and *mercuric nitrate*, but not by *mercuric chloride*, *acetate of copper*, or *nitrate of silver*.

According to Otto, the solution of the soda-salt is precipitated by basic lead acetate immediately, and by the neutral acetate after some time; also by chloride of barium, chloride of calcium, sulphate of magnesia, and nitrate of silver. Taurochenocholic acid is precipitated from the solution of the soda-salt by the stronger mineral acids, but not by acetic, oxalic, or tartaric acid.

Primary Nucleus $C^{54}H^{54}$.

Cerotene.

$C^{54}H^{54}$.

Brodie. *Ann. Pharm.* 67, 210; *Phil. Trans.* 1848, 159.

Cirte (Gmelin).

Chinese wax is distilled, and the distillate is freed from cerotic acid by treating it with potash-ley and boiling with water. The mixture of cerotene and empyreumatic oil then remaining undissolved is purified by pressing, and crystallising, first from a mixture of rock-oil and alcohol, then from ether. — Cerotene is also formed in small quantity by distilling cerotyl-alcohol.

Cerotene resembles paraffin. It melts at 57° to 58°, and solidifies in a crystalline mass (Brodie). Melts at 57·8° and solidifies at 57° (Duffy, *Quart. J. Chem. Soc.* 5, 127).

			Brodie.
54 C	324	85·71	85·40
54 H	54	14·28	14·31
$C^{54}H^{54}$	378	100·00	99·75

Cerotene becomes fluid when *distilled* backwards and forwards in a sealed tube bent at right angles: after six distillations the tube contains inflammable gases and oils, boiling at temperatures varying from 75° to above 260°. — Moist *chlorine* converts it into chlorocerotene (Brodie).

Cerotene melting at 55° dissolves in *ether* more freely than ozocerite (Fritzsche, *J. pr. Chem.* 73, 326).

Cerotylic Alcohol.

$C^{54}H^{56}O^2 = C^{54}H^{54},H^2O^2$.

Brodie. *Ann. Pharm.* 67, 201.

Cerotin.

Occurs in Chinese wax, in combination with cerotic acid.

Preparation. Chinese wax is melted with caustic potash at a gentle heat in an iron vessel; the mass is diffused through boiling water, and the milky liquid is precipitated with chloride of barium. The precipitate of cerotylic alcohol and cerotate of baryta thus thrown down is collected, washed, dried, and powdered, and then boiled with alcohol containing rock-oil, which takes up the cerotylic alcohol together with traces of the baryta-salt. The crystals obtained from this solution are purified by recrystallisation from a mixture of absolute alcohol and ether till their melting point rises to 79°, and until they are free from baryta.

Properties. Crystals melting at 79° (Brodie); melting and solidifying at 81° (Duffy).

			Brodie.
54 C	324	81·81	81·63
56 H	56	14·14	14·20
2 O	16	4·05	4·17
$C^{54}H^{56}O^2$	396	100·00	100·00

Decompositions. 1. Cerotylic alcohol volatilises when strongly *heated*, with little explosions, due to the formation of water, and yields a colourless solid distillate, melting at 70°, and separable by crystallisation from ether, into cerotene and undecomposed cerotylic alcohol. — *Chlorine* converts fused cerotylic alcohol into chlorocerotal:

$$C^{54}H^{56}O^2 + 28Cl = C^{54}Cl^{13}H^{41}O^2 + 15HCl.$$

Cerotylic alcohol is coloured by *oil of vitriol* and decomposed on warming, but in the finely divided state it forms cerotyl-sulphuric acid. — Cerotylic alcohol strongly heated with *potash-lime* is converted into cerotic acid, with elimination of hydrogen.

Cerotic Acid.

$$C^{54}H^{54}O^4 = C^{54}H^{54},O^4.$$

PROUST. *A. Gehl.* 1, 504.
JOHN. *Dessen Chemische Schriften*, 4, 38.
BUCHHOLZ & BRANDES. *Repert.* 4, 145.
BOUDET & BOISSENOT. *J. Pharm.* 13, 38; *Mag. Pharm.* 18, 52.
ETTLING. *Ann. Pharm.* 2, 265.
LEWY. *N. Ann. Chim. Phys.* 13, 438; *J. pr. Chem.* 36, 65; abstr. *Compt. rend.* 16, 675; 20, 38.
BRODIE. *Phil. Trans.* 1848, 1,147; *Phil. Mag.* 33, 217; *J. pr. Chem.* 45, 335; *Ann. Pharm.* 67, 180; abstr. *N. J. Pharm.* 15, 145.— *Phil. Trans.* 1848, 1, 159; *Ann. Pharm.* 67, 199; *Phil. Mag.* 33, 378; *J. pr. Chem.* 46, 30; abstr. *Kopp's Jahresber.* 1847 and 1848, 701.
MASKELYNE. *Quart. J. Chem. Soc.* 5, 24; abstr. *Kopp's Jahresber.* 1852, 525.

Acide sinésique (Lewy).

John distinguished the portion of bees'-wax more easily soluble in alcohol from the less easily soluble myricin, by the name *cerin.* Brodie found it to be an acid, and prepared it in the pure state.

The products formed by the action of *caustic potash* on the cerin of the older chemists are described as *ceraïn*, *margaric acid*, *ceric acid*, and *stearic acid.*

a. According to Boudet & Boissenot, cerin splits up on boiling with potash-ley into margaric acid and non-saponifiable ceraïn, the latter of which forms (after being freed from margaric acid by exhaustion with alcohol) a hard, brittle substance, melting above 70°, and unalterable by alkalis. According to Ettling, ceraïn is infusible in boiling potash-ley, and contains 78·92 p. c. C., and 13·82 H. According to Brodie's investigations a non-saponifiable product is obtained from cerin only when it contains myricin, and in that case this product is melissic alcohol. See compounds with 60 atoms of carbon. — *b.* According to Lewy, cerin, heated to 220° or 230° with potash-lime, evolves hydrogen, and is converted into stearic acid melting at 70° and containing 76·79 p. c. C., and 12·80 H. When boiled with potash-ley it yields another acid melting at 65° and containing 79·77 p. c. C. and 13·73 H.: Lewy's *ceric acid.* Both acids are doubtless to be regarded as mixtures containing cerotic acid, and probably palmitic and melissic acids, derived from the myricin.

Source. Cerotic acid occurs in bees'-wax, and in combination with cerotylic alcohol, in Chinese insect-wax (Brodie).

The waxy substances occurring in the vegetable kingdom, the general diffusion of which was pointed out by Proust, were formerly regarded as mixtures of cerin and myricin; they have not, however, been sufficiently studied. A similar vegetable wax occurs as a coating on the petals of flowers (Elsner, *Schw.* 65, 165), the leaves of cabbage, poppy, and other plants; on the fruit of *Croton sebiferum*, *Tamex sebifera*, plums, figs, grapes, pomegranates, and lemons; as a coating on the stem of *Ceroxylon Andicola*; in the milk of the cow-tree, in pollen, &c. — Raw silk contains cerin, soluble in strong acetic acid (Mulder, *Pogg.* 37, 609). — Concerning the somewhat more fully investigated waxes, see Myricin; on Chinese insect-wax, p. 139 of this volume.

Formation. 1. By heating cerotylic alcohol with potash-lime (Brodie), or by similar treatment of Chinese wax (Lewy; Maskelyne), in both cases with evolution of hydrogen. — 2. By oxidizing paraffin with bichromate of potash and dilute sulphuric acid, or with nitric acid; in the latter case together with succinic, anchoic, and several other acids (Gill & Meusel, *Chem. Soc. J.* 21, 466).

Preparation. 1. Bees'-wax is boiled 3 or 4 times with fresh portions of strong alcohol; and the precipitate which is deposited from the alcoholic liquids on cooling is collected, and crystallised from boiling alcohol till the melting point rises to 70°. The crystals are dissolved in a large quantity of alcohol to a perfectly clear liquid, and the solution is mixed with alcoholic neutral acetate of lead, boiled, and filtered boiling hot from the bulky precipitate, which is again boiled with alcohol and ether till it ceases to give up anything to these liquids. The lead-salt is decomposed with very strong acetic acid, and the cerotic acid thereby liberated is washed with boiling water, dissolved in absolute alcohol, and allowed to crystallise. The acid thus prepared melts at 78°. It may be further purified by boiling it with potash-ley, precipitating the solution with a large excess of chloride of barium and carbonate of soda, washing the precipitate with ether, decomposing with an acid, and crystallising the product repeatedly from ether and alcohol (Brodie). — 2. The acid deposited from alcoholic solution of bees' wax may also be purified, though with difficulty, by oft-repeated crystallisation from a large quantity of ether.

The cerotic acid formed in the preparation of cerotene and cerotylic acid by the methods above described, p. 134, may be purified by washing the baryta-salt with a mixture of mineral naphtha and ether, decomposing, boiling the liberated acid for some time with water to volatilise adhering naphtha, and crystallising repeatedly from ether (Brodie).

¶ 3. From 300 to 500 grammes of paraffin (melting at 60°) were boiled in a flask with 120 grms. bichromate of potash and 180 grms. sulphuric acid diluted with twice its volume of water, a small quantity of peroxide of manganese being added, which accelerates the reaction. After boiling for three or four days the chromic acid was completely reduced. The cake on the surface was then washed, and boiled with carbonate of soda, and the resulting soap was freed from unaltered paraffin by means of alcohol. The solid soap, separated from the liquid by strong pressure, contained acids melting at about 62°, while the solution retained acids melting at about 40°. On recrystallising the hard soap from weak spirit, the melting point of the acids rose to 65°. The entire quantity was then converted into lead-salts, and these were treated with strong alcohol at the boiling heat, which dissolved a considerable quantity. The acid separated from the undissolved portion melted at 74°—75°; but the melting point rose by repeated crystallisation from alcohol and ether, and finally remained constant at 78°. This acid is cerotic acid; at the same time a number of other acids of the same series were formed, some solid, others liquid and volatile, acetic acid predominating amongst the latter (Gill & Meusel) ¶.

Properties. Granular crystals, melting at 81° (Brodie), 80° (Lewy), 81° to 82° (Maskelyne), 78° (Gill & Meusel). Solidifies to a highly crystalline mass after fusion. Distils unaltered (see below) (Brodie). — Cerin reddens litmus (Lewy).

				Brodie.		
			Lewy.	*a.*	*b.*	*c.*
54 C	324	79·02	78 30	78·80	79·13	78·80
54 H	54	13·17	13·10	13 06	13·20	13·19
4 O	32	7·81	8·60	8·14	7·67	8·01
$C^{54}H^{54}O^4$	410	100·00	100·00	100·00	100·00	100·00

Lewy's acid was obtained by the action of potash-lime on Chinese wax. — *a*, prepared according to 1; *b*, according to 2; *c*, distilled acid. Brodie examined cerotic acid from Chinese wax, with similar results. — Heintz (*Pogg.* 92, 599) supposes pure cerotic acid to have a higher melting point, that found by Brodie not being sufficiently high above the melting point of arachidic acid (xvii, 370). Lewy proposed the formula $C^{72}H^{72}O^6$.

Ettling found cerin to contain 77·73 p. c. C., 13·49 H., and 8 78 O., and to melt at 62·5°. Lewy found 79·1 to 80·38 p. c. C., 13·2 to 13·46 H., and 7·70 to 6·16 O.; he proposed the formula $C^{68}H^{68}O^4$.

Decompositions. Cerotic acid distils unaltered when pure, but when it is submitted to *dry distillation*, mixed with other wax constituents, the distillate consists almost entirely of oil, a little solid substance passing over towards the end of the distillation only. Cerotic acid melting at 70° yielded a distillate composed of two oily layers, the upper of which, amounting to $\frac{19}{20}$ths of the whole, gave up to potash a very little acid, and when dissolved in alcohol left a little paraffin, after the removal of which the greater part distilled between 230° and 250°. This part of the oil contained 84·3 p. c. C., and 14·05 H., the portion distilling at 210°—220° contained 84·17 p. c. C., and 13·73 H., and that distilling at 250°—274° contained 85·37 p. c. C., and 14·5 H. (Brodie). — *Chlorine* converts cerotic into chlorocerotic acid (Brodie). — Heated with *nitric acid*, it yields lepargylic acid (xiii, 374) and other substances. See page 139 (Buckton).

Cerotate of Lead. — Precipitated from the alcoholic acid by neutral acetate of lead (Brodie). Yields cerotinone by dry distillation (Brückner).

			Brodie.
$C^{53}H^{53}O^4$	409	79·73	
Pb	104	20·27	20·48
$C^{54}H^{53}PbO^4$	513	100·00	

Cerotate of Silver. — Precipitated by hot alcoholic nitrate of silver from a boiling alcoholic solution of the acid mixed with excess of ammonia (Brodie).

			Brodie.				Gill &
Dried over the water-bath.			*a.*	*b.*	*c.*	*d.*	Meusel.
54 C	324	62·66	62·23	62·51	62·81	62·21	62·36
53 H	53	10·25	10·20	10·32	10·25	10·18	10·31
4 O	32	6·19	6·56	6·48	6·56	6·19	6·21
Ag	108	20·90	21·01	20·69	20·38	21·42	20·92
$C^{54}H^{53}AgO^4$.	517	100·00	100·00	100·00	100·00	100 00	100·00

a was obtained from bees'-wax; *b*, by heating cerotene with potash-lime; *c*, by saponification; and *d*, by dry distillation.

Cerotic acid is soluble in *alcohol* and *ether*. — Cerin dissolves easily in hot *oil of turpentine*, crystallising on cooling (John).

Cerotylsulphuric Acid.

$$C^{54}H^{56}SO^5 = C^{54}H^{56}O^2,SO^3.$$

BRODIE. *Ann. Pharm.* 67, 204.

Cerotylic alcohol, crystallised from ether, and thereby obtained in a more finely divided state, is dried between bibulous paper and made into a pulp with cold oil of vitriol. After standing for two or three hours, the pulp is diluted with water, and the product is washed with water till the washings appear turbid, as is the case when the free sulphuric acid is completely removed. The remaining compound is dried in a vacuum, and crystallised from ether.

Cerotylsulphuric acid dissolves completely in water, with especial facility in water to which the smallest quantity of alcohol is added, and remains as a soft wax on spontaneous evaporation of the solution.

			Brodie.
54 C	324	74·31	74·33
56 H	56	12·84	13·00
S	16	3·68	
5 O	40	9·17	
$C^{54}H^{56}SO^5$	436	100·00	

Gerhardt (*Compt. chim.* 1849, 54) doubts the correctness of this unusual formula.

Cerotate of Ethyl.

$$C^{58}H^{58}O^4 = C^4H^5O,C^{54}H^{53}O^3.$$

Brodie. *Ann. Pharm.* 67, 189.

Cerotinäther.

Obtained by passing hydrochloric acid gas into a solution of cerotic acid in absolute alcohol.

Waxy looking body, melting at 59° to 60° (Brodie), melting at 60·3° and solidifying at 60° (Duffy, *Quart. J. Chem. Soc.* 5, 197).

			Brodie. *mean.*
58 C	348	79·45	79·46
58 H	58	13·24	13·08
4 O	32	7·31	7·46
$C^4H^5O,C^{54}H^{53}O^3$	438	100·00	100·00

Cerotinone.

$$C^{106}H^{106}O^2 = C^{54}H^{54}O^2,C^{52}H^{52}.$$

Brückner. *J. pr. Chem.* 57, 17.

Cerotate of lead is submitted to dry distillation, the process being continued as long as the white fumes condense in a white tallowy mass. The distillate is purified by crystallisation from boiling absolute alcohol and ether, whereby products melting at 62° and at 50° are obtained.

White pearly laminæ. — With chromic acid it evolves carbonic acid and an odour of butyric acid. — Dissolves freely in cold ether.

			Brückner. *a.*	 *b.*
106 C	636	83·90	83·67	83·32
106 H	106	13·99	14·15	14·18
2 O	16	2·11	2·18	2·50
$C^{106}H^{106}O^2$	758	100·00	100·00	100·00

a melted at 62°, *b* at 50°.

Cerotate of Cerotyl.

$$C^{108}H^{108}O^4 = C^{54}H^{55}O,C^{54}H^{53}O^3.$$

LEWY. *N. Ann. Chim. Phys.* 13, 445.
BRODIE. *Ann. Pharm.* 67, 199.

Cerotincirtester, Gm.

The principal constituent of the *Chinese insect-wax*, produced by the puncture of *Coccus sinensis* or *C. ceriferus* on various species of *Rhus*, *Ligustrum*, and *Hibiscus*, or of *Coccus Pela* on *Fraxinus chinensis.*— Chinese wax is white, highly crystalline, harder and more brittle and fibrous than spermaceti. It melts at 83°, emitting an odour of bees-wax and tallow. It is very slightly soluble in boiling alcohol of sp. gr. 0·837 and in boiling ether; insoluble in cold ether, but soluble in rock-oil at 60°, and in oil of turpentine and rape-oil at 70° (Martius, *N. Repert.* 3, 289; Hanbury, *N. J. Pharm.* 24, 136; 36, 318; *N. Jahrb. Pharm.* 19, 286).

To prepare cerotate of cerotyl, Chinese wax is purified by crystallising it from a mixture of alcohol and mineral naphtha, washing the crystals with ether, boiling with water, and recrystallising from absolute alcohol (Brodie).

After purification it melts at 82° (Brodie).

			Lewy.	Brodie.
108 C	648	82·23	80·66	82·23
108 H	108	13·71	13·31	13·58
4 O	32	4·06	6·03	4·19
$C^{54}H^{55}O,C^{54}H^{53}O^3$	788	100·00	100·00	100·00

Lewy proposed the formula $C^{72}H^{72}O^4$.

Breaks up on *dry distillation* into cerotene and cerotic acid (Brodie). Before purification it yields a trace of acrolein (Brodie).—It is scarcely attacked by boiling potash-ley, but when melted with solid *caustic potash* it is resolved into cerotic acid and cerotylic alcohol (Brodie). When strongly heated with potash-lime, it is completely converted into cerotic acid (Maskelyne).—Chinese wax is decomposed by heating with *nitric acid* according to xiii, 374, with formation of butyric, œnanthylic, and caprylic acids, as well as of pimelic, suberic, and lepargylic acids (Buckton). On the identity of lepargylic acid with azelaic acid, see xvii, 79.

Chlorine-nucleus $C^{54}Cl^{12}H^{42}$.

Chlorocerotic Acid.

$$C^{54}Cl^{12}H^{42}O^4 = C^{54}Cl^{12}H^{42},O^4.$$

BRODIE. *Ann. Pharm.* 67, 190.

Melted cerotic acid is exposed to the action of chlorine gas for some days, or so long as hydrochloric acid continues to be evolved, whereby the acid is converted into a transparent pale-yellow thick gum, which may be drawn out in threads.

			Brodie. *mean.*
54 C	324	39·32	39·79
12 Cl	426	51·69	51·34
42 H	42	5·09	5·10
4 O	32	3·90	3·77
$C^{54}Cl^{12}H^{42}O^4$	824	100·00	100 00

It forms with *soda* a salt which is nearly insoluble in water and decomposes on drying over the water-bath.—*Chlorocerotate of ethyl* is obtained in the same way as the cerotate: it resembles chlorocerotic acid.

Chlorocerotate of ethyl.			Brodie.
58 C	348	40·84	40·94
12 Cl	426	50·00	50·68
46 H	46	5·41	5·24
4 O	32	3·75	3·14
$C^4H^5O,C^{54}Cl^{12}H^{41}O^3$	852	100·00	100·00

Chlorocerotal.

$$C^{54}Cl^{13}H^{41}O^2 = C^{54}Cl^{13}H^{41},O^2.$$

BRODIE. *Ann. Pharm.* 67, 205.

Chlorocerotic aldehyde.—Allied to chloral (ix, 200).

Dry chlorine gas is passed for some days over cerotylic alcohol melted in a water-bath, and the mass is boiled with water and dried over the water-bath.

Transparent pale-yellow resin, becoming strongly electric when rubbed.

			Brodie. *mean.*
[illegible]	324	[illegible]	[illegible]
40·5 H	40·5	4·79	4·73
13·5 Cl	479·2	55·20	55·10
2 O	16	1·89	2·41
$C^{54}Cl^{13\cdot5}H^{40\cdot5}O^2$	859·7	100·00	100·00

It is difficult to perceive when the action of the chlorine ceases (Brodie).

Chlorine-nucleus $C^{54}Cl^{22}H^{32}$.

Chlorocerotene.

$$C^{54}Cl^{22}H^{32},$$

BRODIE. *Ann. Pharm.* 67, 210.

When cerotene melted in a water-bath is exposed to a current of moist chlorine for some weeks, it is converted first into a gummy body, then into a transparent resin, which cracks on cooling.

				Brodie.	
			a.	*b.*	*c.*
54 C	324	28·76	31·46	29·47	28·53
22 Cl	781	68·40			
32 H	32	2·84	3·54	3·00	2·84
$C^{54}Cl^{22}H^{32}$	1137	100·00			

a and *b* had been exposed to the action of chlorine for a shorter time than *c*.

COMPOUNDS CONTAINING 56 ATOMS OF CARBON.

Geoceric Acid.

$$C^{56}H^{56}O^4 = C^{56}H^{56},O^4.$$

Obtained from lignite by Brückner. Supposing the above formula to be correct, the body would belong to this place. See xvii, 445.

COMPOUNDS CONTAINING 60 ATOMS OF CARBON.

Primary Nucleus $C^{60}H^{52}$; *Oxygen-nucleus* $C^{60}H^{46}O^6$.

Caïncetin.

$$C^{60}H^{46}O^8 = C^{60}H^{46}O^6,O^2.$$

ROCHLEDER. *Wien. Acad. Ber.* 45, 7; *J. pr. Chem.* 85, 286.

The product formed by the complete elimination of sugar from caïncin (and chiococcic acid).

Caïncin is dissolved in alcohol of sp. gr. 0·824; and the solution, mixed with hydrochloric acid and absolute alcohol, is heated for eight hours in a water-bath, with frequent addition of alcohol, and afterwards heated, with addition of water, till the whole of the alcohol is expelled. In this way yellow gelatinous flocks are formed, sugar remaining in solution. The flocks are dissolved in excess of alcoholic potash by the heat of a water-bath; the solution is mixed with water; and the alcohol is driven off, whereupon caïncetin-potash is deposited in needles, which are collected, pressed, and recrystallised from alcohol containing potash. From these needles water abstracts the potash, leaving caïncetin.

Properties. Caïncetin is occasionally obtained from alcohol in distinct crystals, but generally in gelatinous lumps made up of microscopic crystals.

	at 130°.		Rochleder.
60 C	360	76·60	76·35
46 H.	46	9·79	9·82
8 O	64	13·61	13·83
$C^{60}H^{46}O^8$	470	100·00	100·00

Homologous with sapogenin, $C^{56}H^{42}O^8$ (xvi, 89 *d*) Rochleder).

Caïncetin breaks up when melted with *caustic potash*, apparently yielding butyric acid, and a potash-salt which is insoluble in alkaline water, and contains [after deduction or separation of the potash? (Kr.)] 74·27 to 75·20 p. c. C., and 10·80 to 10·86 H., probably the salt of an acid represented by the formula $C^{52}H^{42}O^{8}$ (calc. 74·46 p. c. C., 10·05 H.) (Rochleder).

Caïncetin-potash. Dazzling-white, silky, delicate needles, which dissolve in caustic potash and are decomposed by water.

Dried at 118° *in air-current.*			Rochleder.	
60 C	360	69·63	69·33	69·58
46 H	46	8·90	8·91	9·08
8 O	64	12·38	12·67	12·42
KO	47·1	9·09	9·09	8·92
$C^{60}H^{46}O^{8},KO$	517·1	100·00	100·00	100·00

The above is Rochleder's formula, according to which the salt is formed without elimination of water.

Caïncetin-baryta.—A solution of the potash-salt in weak spirit throws down from chloride of barium a white crystalline precipitate, which becomes highly electric when rubbed in the dry state.

Dried at 107° *in air-current.*			Rochleder.
60 C	360	64·80	64·59
47 H	47	9·46	8·51
9 O	72	12·95	13·38
BaO	76·6	13·79	13·52
$C^{60}H^{47}O^{9},BaO$	555·6	100·00	100·00

Rochleder's formula.

Caïncetin dissolves in hot, more freely than in cold *alcohol*: water converts the solution into a transparent jelly.

Glucosides of Caïncetin.

Chiococcic Acid.

$$? \; C^{72}H^{54}O^{16} = C^{60}H^{44}O^{6},C^{12}H^{10}O^{10}.$$

ROCHLEDER & HLASIWETZ. *Wien. Acad. Ber.* 5, 11; *J. pr. Chem.* 51, 415.
ROCHLEDER. *Wien. Acad. Ber.* 45, 7; *J. pr. Chem.* 85, 285.

Produced by the partial splitting up of caïncin by acids (or alkalis) p. 144.

Caïncin is boiled with dilute acids; the flocks thereby precipitated are dissolved in boiling weak spirit; and the solution is cooled, whereupon nearly the whole of the acid is deposited if the alcohol is not too strong. The acid is collected on linen, pressed, and purified by dissolving it in alcohol and precipitating with water.

Properties. White, translucent, horny, friable mass, turning yellowish-grey at 100°. When freshly precipitated it resembles gelatinous silica. Tastes very bitter.

Three months in a vacuum.			Rochleder & Hlasiwetz.
72 C	432	68·35	68·40
56 H	56	8·86	8·83
18 O	144	22·79	22·77
$C^{72}H^{56}O^{18}$	632	100·00	100·00

Dried at 120°.			Rochleder & Hlasiwetz.
72 C	432	70·36	70·18
54 H	54	8·80	8·98
16 O	128	20·84	20·84
$C^{72}H^{54}O^{16}$	614	100·00	100·00

The above are Rochleder's formulæ. He and Hlasiwetz proposed the earlier formulæ $C^{12}H^{9}O^{3}$ and $C^{48}H^{35}O^{11}$. Hlasiwetz (*Wien. Acad. Ber.* 6, 278) formerly regarded chiococcic acid as identical with kinovin, but afterwards (*Ann. Pharm.* 111, 182) doubted the identity of the two bodies, which has been rendered still less probable by the researches of Rochleder. The latter chemist now regards chiococcic acid as homologous with a product formed by the partial breaking up of saponin according to xvi, 89 c.

Decompositions. Chiococcic acid carbonises when *heated,* yielding a small quantity of a shining sublimate, a thick oil smelling of incense and petroleum, and an acid distillate. — It dissolves with red colour in *oil of vitriol* (Hlasiwetz). — Heated with alcoholic *hydrochloric acid,* it breaks up into caïncetin and sugar:

$$C^{72}H^{56}O^{18} + 2HO = C^{60}H^{46}O^{8} + C^{12}H^{12}O^{12} \text{ (Rochleder).}$$

Chiococcic acid is insoluble in *water.* — It dissolves in aqueous *alkalis.* — The alcoholic solution gives with *neutral acetate of lead* a white precipitate, which, after washing with alcohol and drying at 100°, contains 42·96 p. c. C., 5·30 H., 14·03 O., and 37·71 PbO.

It dissolves in *alcohol* and is precipitated in the form of a jelly by water.

Caïncin or Caïncic Acid.

$$C^{120}H^{91}O^{53} = C^{60}H^{46}O^{8},5C^{12}H^{9}O^{9}.$$

François, Pelletier & Caventou. *J. gen. de méd.* 111, 150; *J. Pharm.* 16, 465; abstr. *Ann. Chim. Phys.* 44, 291; *Repert.* 36, 263.
Liebig. *Pogg.* 21, 33; *Ann. Chim. Phys.* 47, 185.
Rochleder & Hlasiwetz. *Wien. Acad. Ber.* 5, 8; *J. pr. Chem.* 51, 415; abstr. *Ann. Pharm.* 76, 238; *Repert.* 108, 97.
Rochleder. *Wien. Acad. Ber.* 45, 7; *J. pr. Chem.* 85, 284.

Acide kahincique.

Source. In the bark of the root of *Chiococca racemosa* (*Handbuch,* viii, 56) in which it exists as acid caïncate of lime (François, Pelletier

& Caventou). The official *Tinctura Caincæ* deposits, on standing, crystals of a mixture of caïncic acid and its lime-salt (Landerer, *Pharm. Viertelj.* 6, 65).

Preparation. — 1. The root is exhausted by repeated treatment with alcohol of sp. gr. 0·85 ; the tinctures are freed from alcohol by distillation ; the residue is evaporated and dissolved in water, which leaves behind fat and a brown powder ; the aqueous filtrate is completely precipitated with basic acetate of lead ; the precipitate is washed with boiling water and decomposed under water by hydrosulphuric acid ; the sulphide of lead, which contains the whole of the caïncic acid, is dried and boiled with alcohol ; and the alcoholic liquid is filtered, decolorised with animal charcoal, and evaporated till it crystallises. — Or the alcoholic extract may be dissolved in water, the filtrate precipitated with excess of lime, and the precipitated basic caïncate of lime decomposed with alcoholic oxalic acid (François, Pelletier & Caventou).

2. An alcoholic decoction of the root-bark is precipitated with alcoholic neutral acetate of lead ; the precipitate, which consists of caffetannate with a little caïncate of lead, is separated ; the filtrate is precipitated with basic acetate of lead ; and the liquid filtered from sulphide of lead is evaporated to crystallisation. If the precipitate produced by neutral acetate of lead be decomposed by hydrosulphuric acid, and the filtrate, freed from hydrosulphuric acid, again precipitated with the neutral acetate and filtered, the filtrate gives with basic acetate of lead a precipitate of caïncate of lead, from which caïncic acid may be obtained by decomposing it with hydrosulphuric acid, and evaporating the filtrate.
The crystals thus obtained are purified by pressing and recrystallising from weak spirit (Rochleder & Hlasiwetz).

Properties. White, silky, slender, felted needles, inodorous, tasteless at first, but afterwards very bitter and styptic. Permanent in the air. Reddens litmus (François, Pelletier & Caventou).

			Liebig.	Rochleder & Kavalier.	Kavalier.	Rochleder.
120 C	720	58·30	56·74	58·25	57·31	58·24
91 H	91	7·36	7·48	7·75	7·87	7·38
53 O	424	34·34	35·78	34·00	34·82	34·38
$C^{120}H^{91}O^{53}$	1235	100·00	100·00	100·00	100·00	100·00

The caïncin analysed by Liebig lost 9 p. c. more water at 100°. The other analyses (which are given in mean numbers) were made with caïncin dried at 100°, except that of Rochleder, who analysed caïncic acid dried at 110°. — Rochleder & Kavalier proposed the earlier formula $C^{16}H^{13}O^{7}$, for which Rochleder submitted that given above, deduced from the decomposition-products of caïncin. The correctness of this formula is rendered improbable by the uneven numbers of hydrogen and oxygen atoms, and also by the composition of the salts of caïncic acid.

Decompositions. 1. Caïncic acid *heated* in a glass tube softens, carbonises, and evolves white fumes, which partly condense in light crystals (François, Pelletier, & Caventou). — 2. It *burns* when heated, emitting an odour of incense (Rochleder & Hlasiwetz).

3. Caïncic acid dissolves in cold fuming *hydrochloric* acid, and solidifies almost instantaneously to a transparent jelly, from which water throws down white tasteless flocks, the acid mother-liquor then con-

taining no more caïncic acid (François, Pelletier, & Caventou). It is resolved by hydrochloric acid into caïncin-sugar and chiococcic acid, or by the ultimate action of alcoholic hydrochloric acid into caïncin-sugar and caïncetin (p. 141): the latter body being formed by the elimination of 5 atoms, and chiococcic acid by the elimination of 4 atoms of sugar:—

$$C^{120}H^{91}O^{53} + 15HO = \underset{\text{Caïncetin.}}{C^{60}H^{46}O^{8}} + 5C^{12}H^{12}O^{12};$$

$$C^{120}H^{91}O^{53} + 11HO = \underset{\text{Chiococcic acid.}}{C^{72}H^{54}O^{16}} + 4C^{12}H^{12}O^{12} \text{ (Rochleder).}$$

The sugar obtained by boiling 100 parts of caïncin with hydrochloric acid for six hours reduces as much tartrate of copper as 50·54 parts of grape-sugar; at the same time 44·74 parts of jelly (chiococcic acid?) are produced (Rochleder & Kawalier). On boiling caïncic acid for eight hours with alcoholic hydrochloric acid, and afterwards driving off the alcohol, with addition of water, 40·09 p. c. of caïncetin is obtained (by calc. 38·06 p. c. $C^{60}H^{46}O^{8}$) (Rochleder).

The sugar produced in the reaction is of a yellowish colour, and has a sweetish mawkish taste. It smells of caramel when heated, and behaves like grape-sugar towards an alkaline solution of cupric oxide (Rochleder & Hlasiwetz). According to Rochleder's later statements, it is uncrystallisable, and is not identical with dextroglucose.

4. Caïncic acid is decomposed by *oil of vitriol.* — 5. *Nitric acid* acts like hydrochloric acid at first, but afterwards evolves nitric oxide, and produces an artificial bitter, but no oxalic acid. — 6. Caïncic acid dissolves in cold *glacial acetic acid*, remains in the crystalline form when the solution is evaporated in the air, and gelatinizes on warming (François, Pelletier & Caventou). — 7. Caïncic acid, heated with very strong *potash-ley*, froths strongly, evolves gas, and an odour of metacetone, and forms a yellowish-brown mass, which, when supersaturated with acetic acid, evolves carbonic acid and deposits chiococcic acid (Rochleder & Hlasiwetz).

Combinations. Caïncic acid requires for its solution more than 600 parts of *water*, and is very slightly soluble in dilute cold *hydrochloric* and *nitric acids* (François, Pelletier & Caventou).

With bases it forms *caïncates.*

The solution of caïncic acid in *ammonia-water* leaves on evaporation an amorphous pellicle, from which potash expels ammonia. The caïncates of the *alkalis* are bitter and soluble in alcohol; the *potash-salt* is not crystallisable. The solution of caïncic acid in *baryta-water* leaves no crystals when evaporated (François, Pelletier, & Caventou).

Caïncate of lime. — Caïncic acid forms with lime-water a clear solution, from which more lime-water throws down basic caïncate of lime in white, strongly alkaline flocks (François, Pelletier & Caventou). — The alcoholic extract of the root-bark of *Chiococca racemosa* contains caïncate of lime, which, when caïncic acid is prepared according to p. 144, remains in the mother-liquor, and may be precipitated in white flocks by anhydrous alcohol. These flocks, after drying at 100°, contain, on the average, 50·37 p. c. C., 7·60 H., 36·50 O., and 5·58 CaO (Rochleder & Hlasiwetz).

Caincate of lead.—*a.* Aqueous caïncic acid gives an abundant white slimy precipitate with basic acetate of lead. The precipitate contains 26·60 p. c. C., and 51·40 p. c. PbO. (Rochleder & Hlasiwetz). —*b.* Alcoholic caïncic acid throws down from alcoholic neutral acetate of lead, a slight precipitate containing, after drying at 100°, 34·95 p. c. C, 4·45 H., 20·30 O., and 40·30 PbO., or 16 atoms C. to 1 atom PbO (Rochleder & Hlasiwetz).

Caincic does not precipitate *ferric salts* (Rochleder & Hlasiwetz).

It dissolves more freely in hot than in cold *alcohol*, crystallising on cooling. In *ether* it is not more freely soluble than in water (François, Pelletier & Caventou).

¶ According to more recent researches by Rochleder (*J. pr. Chem.* cii, 18), caïncic acid dried at a temperature near 100° has the composition $C^{80}H^{64}O^{36}$, but by prolonged drying it loses a little more water, and then exhibits the composition—

$$C^{160}H^{126}O^{70} = C^{80}H^{64}O^{36},C^{80}H^{62}O^{34}.$$

near 100°.			Kawalier.	*After prolonged drying.*		Rochleder & Hlasiwetz, *mean.*
80 C	480	57·69	57·41	160 C	58·32	58·23
64 H	64	7·69	7·86	126 H	7·66	7·75
36 O	288	34·62	34·73	70 O	34·02	34·02
$C^{80}H^{64}O^{36}$	832	100·00	100·00		100 00	100·00

Caïncetin has the composition $C^{44}H^{34}O^{6}$.

			Rochleder.
44 C	264	76·30	76·35
34 H	34	9·83	9·82
6 O	48	13·87	13·83
$C^{44}H^{34}O^{6}$	346	100·00	100·00

Its formation by the decomposition of caïncic acid is represented by the equation—

$$C^{80}H^{64}O^{36} + 6HO = C^{44}H^{34}O^{6} + 3C^{12}H^{12}O^{12}.$$

According to this equation, the quantity of caïncetin produced should be 41·59 p. c.; Rochleder & Kawalier obtained 40·09 p. c.

The compounds of caïncetin with potash and baryta above described (p. 145) are merely mixtures; the potash-compound may be represented empirically by the formula: $4C^{44}H^{34}O^{6},3KO$, which requires 69·23 p. c. C., 8·92 H., 12·59 O., and 9·26 KO., and the baryta-compound by $4C^{44}H^{34}O^{6}.3BaHO^{2}$, which requires 64·36 p. c. C., 8·47 H., 13·16 O., and 14·01 BaO. True salts of caïncetin do not appear to exist.

Caïncigenin, $C^{28}H^{24}O^{4}$, is formed, together with butyric acid, by fusing caïncetin with hydrate of potash—

$$C^{44}H^{34}O^{6} + 6HO = C^{28}H^{24}O^{4} + 2C^{8}H^{8}O^{4}.$$

The portion of the product insoluble in aqueous potash is a compound of caïncigenin with potash, from which the caïncigenin may be separated by hydrochloric acid.

	at 130°.		Rochleder.
28 C	168	75·00	75·18
24 H	24	10·71	10·80
4 O	32	14·29	14·02
$C^{28}H^{24}O^{4}$	224	100·00	100·00

Caïncigenin is homologous with æscigenin (p. 31), and with the substance $C^{22}H^{18}O^{4}$, sometimes found in horse-chestnut seeds. It resembles æscigenin in its physical properties and its relations to solvents.

When caïncic acid is treated with sodium-amalgam and aqueous alcohol, it dissolves to a brownish liquid, from which dilute sulphuric acid separates a crystalline substance, $C^{72}H^{58}O^{30}$, which, after washing with water and pressing between linen and filter-paper, forms a white mass having a strong silky lustre.

	Dried at 100° *in a stream of carbonic acid.*		Rochleder.	
72 C	432	59·18	59·02	59·23
58 H	58	7·95	8·06	8·09
30 O	240	32·87	32·92	32·68
$C^{72}H^{58}O^{30}$	730	100·00	100·00	100·00

The formation of this substance from caïncic acid is represented by the equation—

$$C^{80}H^{64}O^{36} + 4H = C^{72}H^{58}O^{30} + C^{8}H^{8}O^{4} + 2HO.$$

Caïncin. Crystalline substance. Butyric acid.

By dissolving this compound in alcohol, adding fuming hydrochloric acid, and heating for eight hours in the water-bath, it is converted into a gelatinous substance, $C^{36}H^{28}O^{4}$, more soluble in ether than in alcohol.

	Dried at 120° *in a stream of carbonic acid.*		Rochleder.	
36 C	216	78·26	78·39	78·34
28 H	28	10·15	10·18	10·49
4 O	32	11·59	11·43	11·17
$C^{36}H^{28}O^{4}$	276	100·00	100·00	100·00 ¶

Azo-nucleus $C^{60}N^{2}H^{44}O^{6}$.

Jervine.

$$C^{60}N^{2}H^{46}O^{6} = C^{60}N^{2}H^{44}O^{6},H^{2}.$$

Ed. Simon. *Pogg.* 41, 569; *Ann. Pharm.* 24, 214.—*N. Br. Arch.* 29, 186.

Will. *Ann. Pharm.* 35, 116.

Discovered by Simon in *Radix Hellebori albi.* Does not occur in sabadilla seeds.

Preparation. The alcoholic extract is boiled repeatedly with water containing hydrochloric acid; the clear filtrate is precipitated with carbonate of soda free from sulphate; the precipitate is dissolved in alcohol; the alcoholic solution is decolorised with animal charcoal; and most of the alcohol is distilled off: the residue then crystallises on cooling. The crystals are pressed (whereby most of the veratrine is separated), moistened with alcohol, and again pressed, jervine then remaining tolerably pure. Besides veratrine, the mother-liquor contains jervine, which may be recovered by evaporating and boiling the residue with dilute sulphuric acid. Sulphate of jervine then remains undissolved, and may be decomposed by boiling with carbonate of soda (Simon).

Properties. The white crystals, dried in the air, contain 6·88 p. c. water (4 at. = 6·95 p. c. HO), which they lose at 100°. It melts to a clear oil when heated, does not decompose at 190°, but turns brown above 200°, and burns with a smoky flame (Will).

	at 100°.		Will. *mean.*
60 C	360	74·68	74·73
2 N	28	5·83	5·38
46 H	46	9·54	9·62
6 O	48	9·95	10·27
$C^{60}N^2H^{46}O^6$	482	100·00	100·00

The above is Limpricht's formula (*Lehrb.* 1190). Will's formula is $C^{60}N^2H^{45}O^5$.

Jervine is nearly insoluble in *water* (Will). It forms with *phosphoric acid* an easily soluble salt, and with *hydrochloric*, *nitric*, and especially *sulphuric acid*, salts which are sparingly soluble in water and alcohol, and are precipitated by those acids from the phosphate, and from the equally easily soluble *acetate* (Simon). *Ammonia* throws down from acetate of jervine, bulky flocks, soluble with difficulty in excess of the precipitant (Will). Jervine is precipitated in bright-yellow flocks by *phosphomolybdic acid* (Sonnenschein).

Chloroplatinate of Jervine. Obtained by precipitating acetate or alcoholic hydrochlorate of jervine with bichloride of platinum, evaporating, and washing the salt with water. — Fine bright-yellow flocks (Will).

		Will.
$C^{60}N^2H^{46}O^6$	482	70·03
HCl,Cl^2	107·5	15·62
Pt	98·7	14·35
$C^{60}N^2H^{46}O^6,HCl,PtCl^2$	688·2	100·00

Jervine is insoluble in *alcohol* (Will).

Primary Nucleus $C^{60}H^{54}$; *Oxygen-nucleus* $C^{60}H^{36}O^{18}$.

Coriamyrtin.

$C^{60}H^{36}O^{20} = C^{60}H^{36}O^{18},O^{2}$.

RIBAN. *Par. Soc. Bull.* [2] 7, 79; *Compt. rend.* 63, 476, and 680; abstr. *Krit Zeitschr.* 9, 663.

See xvii, 368. Riban replaces the formula there given by the above.—Coriamyrtin is not a glucoside.

Properties. For crystalline form, see xvii, 368. It rotates a ray of polarised light to the right; [α]j = 24·5°.

			Riban.	
60 C	360	64 75	63 9	64 2
36 H	36	6 47	6·5	6 6
20 C	160	28·78	29·6	29 2
$C^{60}H^{36}O^{20}$	556	100·00	100·0	100·0

Coriamyrtin is dissolved and carbonised by *oil of vitriol.* Fuming *nitric acid* produces a small quantity of an amorphous nitro-compound.—It is not attacked by dry *hydrochloric acid gas*, even at 100°. On boiling it with weak aqueous hydrochloric acid, yellow flocks are produced. The filtrate reduces alkaline solution of cupric oxide, and contains two resins, one of which is soluble in ether, but no sugar.—Fuming *hydriodic acid* decomposes coriamyrtin in the cold, and more quickly at 100°, with separation of iodine, and formation of a black soft substance which, when washed with water and dissolved in alcohol, gives with alkalis an intense purple coloration.—*Bromine* dropped into alcoholic coriamyrtin throws down *bibromocoriamyrtin*, $C^{60}Br^{2}H^{34}O^{20}$, which crystallises from boiling alcohol in fine needles, containing 50·3 p. c. C., 4·9 H., and 22·35 Br. (calc. 50·4 p. c. C., 4·8 H., 22·4 Br.).—*Chlorine* produces several crystallisable substitution-compounds.

Aqueous *alkalis* colour coriamyrtin brown. *Baryta-* and *lime-water* form with it yellow amorphous salts (with assimilation of 12 atoms of water), which are easily soluble in water, sparingly soluble in cold alcohol, insoluble in ether, and the acid of which is thrown down by sulphuric or oxalic acid as an amorphous precipitate soluble in water. The baryta-salt, $C^{60}H^{46}Ba^{2}O^{32}$, contains on the average 44·85 p. c. C., 5·8 H., and 16·9 Ba. (by calc. 45·1 p. c. C., 6·7 H., 17·1 Ba.); the lime-salt, $C^{60}H^{46}Ca^{2}O^{32}$, 50·45 p. c. C., 6·6 N., and 5·9 Ca. (calc. 50·3 p. c. C., 6·5 H., 5·7 Ca.).

When coriamyrtin is heated to 140° with *acetic anhydride* for an hour, and the product is washed with water, a soft body, afterwards falling to a powder, is obtained, which, when dissolved in alcohol and evaporated, remains as an amorphous brittle mass. It contains 58·45 p. c. C., and 6·3 H., and when decomposed with alkalis yields an amount of acetate corresponding to 34·3 p. c. of acetic anhydride, and is therefore represented by the formula $C^{84}H^{54}O^{38} = C^{60}H^{36}O^{20} + 3C^{8}H^{6}O^{6}$ (Riban) (calc. 58·5 p. c. C., 6·3 H., 35·5 p. c. acetic anhydride).

Primary Nucleus $C^{60}H^{60}$.

Melene.

$C^{60}H^{60}$.

ETTLING. *Ann. Pharm.* 2, 255.
BRODIE. *Ann. Pharm.* 71, 156.

Discovered by Ettling, who, however, mistook it for paraffin.

Formation. By the dry distillation of melissic alcohol and myricir (Brodie), or of bees'-wax (Ettling).

Preparation. Myricin is subjected to dry distillation; the distillate is freed from palmitic acid by treating it with potash-ley; and the melene which floats on the surface of the liquid is pressed between blotting-paper, rectified over potassium, again pressed, and crystallised from ether (Brodie). — Bees'-wax submitted to dry distillation yields amongst other products, a solid distillate, wax-butter. When this is pressed and melted with hot water, and afterwards boiled with potash-ley, there separates an oily body, which solidifies on cooling, and is to be boiled with water and crystallised from 90 p. c. alcohol. As thus prepared it contains an oxygenated compound, which may be decomposed by heating with oil of vitriol, after which ether will extract from the carbonaceous mass the purer melene (Ettling).

Properties. Colourless crystals, melting at 62° (Brodie), and appearing translucent and lustrous after fusion (Ettling). Volatilises below its boiling-point.

			Ettling.	Brodie.
60 C	360	85·72	84·24	85·31
60 H	60	14·28	14·92	14·44
$C^{60}H^{60}$	420	100·00	99·16	99 75

To this place probably belongs a product obtained from wax (by dry distillation ?) and examined as paraffin by Lewy. It contains on the average 84·91 p. c. C., 14 90 H. [= $C^{20}H^{21}$ (Lewy)], melts at 46·8°, and boils at 370° to 380°; its sp. gr. is 0·89, and its vapour-density 10 to 11·8 (Lewy, *N. Ann. Chim. Phys.* 5, 395).

Decompositions. 1. Melene is not attacked by cold *nitric acid* of sp. gr. 1·25, and distils unchanged with the boiling liquid. — 2. When heated with *oil of vitriol*, it slowly turns yellow, then brown. On boiling it with oil of vitriol a portion of the melene is carbonised, a second portion volatilises, and the remainder may be extracted by ether from the washed residue in its original state. — 3. Melene, when pure, is not affected by *potash-ley* or by *potassium* (Ettling).

Melissic Alcohol.

$C^{60}H^{62}O^2 = C^{60}H^{60},H^2O^2$.

BRODIE. *Ann. Pharm.* 71, 147; *Phil. Mag.* 35, 246.

Melissin. Myricyl-alcohol. — Occurs in the free state in Canaüba wax (p. 159), and may be dissolved out by alcohol (Maskelyne, *Chem. Soc. J.* [2], vii, 87).

Preparation. From Myricin. Myricin is saponified by boiling with strong potash-ley, or with alcoholic potash, or by melting with caustic potash; the alcohol that may have been employed is distilled off; and the soap, dissolved in boiling water, is decomposed by adding an acid to the boiling solution. The fused mass thereby separated is boiled repeatedly with water, and dissolved in a large quantity of alcohol; and the abundant precipitate formed on cooling is collected on a filter and purified by repeatedly dissolving in alcohol and crystallising, when the palmitic acid also formed at the time of saponification remains in solution. The product is further purified by recrystallising it from rectified coal-oil. — Or the solution of the potash-soap is precipitated by a baryta-salt; the baryta-soap is exhausted with ether; and the substances taken up thereby are crystallised repeatedly from ether or alcohol, till the melting-point rises to 70° to 80°. Pure melissic alcohol, in very small quantity, is obtained only by collecting apart that portion which crystallises from the ethereal solution when partially cooled by means of a heated funnel. — Bees-wax or Ceylon wax may be employed, instead of myricin, for the preparation of melissic alcohol (Brodie). Also Canauba wax (Maskelyne).

Properties. Crystalline silky mass, melting at 85° (Brodie), about 88° (Maskelyne), and solidifying in a fibrous crystalline mass on cooling.

			Brodie. *mean.*	Maskelyne. *mean.*
60 C	360	82·19	82·33	82·48
62 H	62	14·15	14·11	14·24
2 O	16	3·66	3·56	3·28
$C^{60}H^{62}O^{2}$	438	100·00	100·00	100·00

The analyses agree more nearly with the formula $C^{62}H^{64}O^{2}$, which requires 82·30 p. c. C., 14·16 H., and 3·54 O.

Melissic alcohol submitted to *dry distillation*, distils partly unaltered, and is partly converted into a solid hydrocarbon, with loss of water. — It combines with *oil of vitriol* in the same way as cerotylic alcohol (p. 134). — It is converted into melissic acid by melting it with *potash-lime*. *Chlorine* acts upon it in the same way as upon cerotylic alcohol, forming a resinous body, *chlormelal*, corresponding to chloral.

	Chlormelal.		Brodie. *mean.*
60 C	360·0	38·50	38·67
14·5 Cl	514·8	54·90	54·83
45·5 H	45·5	4·86	4·74
2 O	16·0	1·74	1·76
$C^{60}Cl^{14.5}H^{45.5}O^{2}$	936·3	100·00	100·00

¶ Melissic alcohol (from Canaüba wax) repeatedly treated with *pentachloride* of *phosphorus* yields a substance melting at about 65°, but after heating with water, at 61°. Boiling alcohol extracts from this product a substance which, after two recrystallisations from ether, melts at 65°—66·5°; it appears to be a mixture of the two compounds $C^{60}H^{61}Cl$ (or $C^{62}H^{63}Cl$) and $C^{60}H^{60}Cl^{2}$ (or $C^{62}H^{62}Cl^{2}$) (Maskelyne).

The same alcohol melted in a sulphuric acid bath at 120°—135°; then mixed with a small quantity of phosphorus and excess of *iodine*, and heated for some time to 130°, is converted into *melissic iodide*. On agitating the mass with water at 80°, then drying it and digesting with ether, the iodide remains behind as a mass melting at 67°, while a body melting at 70°—75·5° passes into solution. The iodide yielded by analysis numbers agreeing nearly with either of the formulæ $C^{60}H^{61}I$, or $C^{62}H^{63}I$.

	Calculation.					Maskelyne.	
60 C	360	65·69	62 C	372	66 19	64·56	65·72
61 H	61	11·13	63 H	63	11·21	11·16	11·12
I	127	23·18	I	127	22·60	21 74	
$C^{60}H^{61}I$	548	100·00	$C^{62}H^{63}I$.	562	100·00		

The iodide is not attacked by silver oxide at 120°—130°. It appears to unite with *ammonia* and with *aniline*, forming unstable compounds, from which it is separated on boiling (Maskelyne).

Melissyl-sulphuric acid was prepared by digesting the alcohol with sulphuric acid in a water-bath till it was all dissolved or suspended, then dissolving in alcohol and saturating with alcoholic potash. A copious white precipitate was thereby produced, which, after repeated boiling with water, left a white flocculent residue, nearly insoluble in alcohol and ether, melting at 90°, and agreeing in composition with the formula $C^{62}H^{63}KS^2O^8$ more nearly than with $C^{60}H^{61}KS^2O^8$.

	Calculation.					Maskelyne.	
60 C	360	64·75	62 C	372	65·26	65 69
61 H	61	10·97	63 H	63	11·05	11·27
K	39·1	7·01	K	39·1	6·84	6·74
$2SO^4$	96	17·27	$2SO^4$	96	16·85	16·30
$C^{60}H^{61}KS^2O^8$	556·1	100·00	$C^{62}H^{63}KS^2O^8$	570·1	100·00	100·00¶

Melissic Acid.

$$C^{60}H^{60}O^4 = C^{60}H^{60},O^4.$$

BRODIE. *Ann. Pharm.* 71, 149; *Phil. Trans.* 1849, 94; *Phil. Mag.* 35, 247; *J. pr. Chem.* 48, 387.

Obtained as a crystalline mass, melting at 86° to 89°, by heating melissic alcohol with potash-lime.

			Brodie. *mean.*
60 C	360	79·64	79·66
60 H	60	13·27	13·34
4 O	32	7·09	7·00
$C^{60}H^{60}O^4$	452	100·00	100·00

Melissate of silver is obtained in the same way as the cerotate (p. 137).

			Brodie.
60 C	360	64·38	64·02
59 H	59	10·55	10·77
Ag	108	19·30	19·48
4 O	32	5·77	5·73
$C^{60}H^{59}AgO^4$	559	100·00	100·00

Myricin.

$C^{92}H^{92}O^4 = C^{60}H^{61}O,C^{32}H^{31}O^3$.

John. *Dessen chemische Schriften*, 4, 38.
Buchholz & Brandes. *Repert.* 4, 145.
Boudet & Boissenot. *J. Pharm.* 13, 42.
Ettling. *Ann. Pharm.* 2, 206.
Hess. *J. pr. Chem.* 13, 415.
Van der Vliet. *J. pr. Chem.* 16, 302.
Lewy. *N. Ann. Chim. Phys.* 13, 438.
Brodie. *Phil. Trans.* 1849, 91; *Phil. Mag.* 35, 244; *Ann. Pharm.* 71, 144; *J. pr. Chem.* 48, 391; *N. J. Pharm.* 16, 66; *Kopp's Jahresber.* 1847 and 1848, 704.

Palmitate of melissyl. — John distinguished the portion of bees-wax or myrtle wax, insoluble in alcohol, from the soluble cerin by the name myricin. Brodie first prepared it in the pure state and ascertained its nature.

Source. In bees-wax, especially abundant in that from Ceylon.

Preparation. Bees-wax is boiled with fresh portions of alcohol so long as the decanted solution continues to precipitate neutral acetate of lead, and therefore contains cerotic acid. The crude myricin then remains as a greenish non-crystalline mass, of waxy consistence, having a faint odour of wax, and melting at 64°. It is purified by crystallising it repeatedly from ether, or more quickly from a mixture of coal-oil and ether, and collecting the crystals first deposited from the still warm solution (Brodie).

Properties. Feathery crystals, melting at 72° and solidifying to a highly crystalline mass (Brodie).

			Brodie. *mean.*
92 C	552	81·65	81·54
92 H	92	13·60	13·38
4 O	32	4·75	5·08
$C^{69}H^{61}O,C^{32}H^{33}O^3$	676	100 00	100·00

To be regarded as palmitate of melissyl (Brodie).

Crude myricin is harder and more brittle than cerin (John); very hard, brittle, and but slightly plastic (Ettling); of the consistence of wax and not crystalline. Sp. gr. 0·9 at 19° (John), 1·0 (Buchholz & Brandes). Melting-point of the investigated product 35° to 37·5° (John); 58·7°, solidifying at 58° (Ettling); 65° (Boudet & Boissenot; Hess). Solidifies at 60·5° (Lewy).

Analyses of crude Myricin.

			Van der Vliet.		Lewy.	
	Ettling.	Hess.	*a.*	*b.*	*a.*	*b.*
C	79·50	79·93	80·54	79·35	80·23	80·28
H	13·80	13·30	13·54	13·06	13·33	13·22
O	6·70	6·77	5·92	7·59	6·44	6·50
	100·00	100·00	100·00	100·00	100·00	100·00

a myricin from yellow wax; *b* from white wax.

Decompositions of crude myricin. 1. When submitted to *dry distillation* it emits an odour of butyric acid, which is the fainter the more carefully the myrin is exhausted with boiling alcohol. The distillate consists at first of fatty acids, amongst which palmitic acid predominates, and afterwards of hydrocarbons rich in melene (Brodie). Volatilises almost entirely undecomposed, a small portion being converted into acetic acid, empyreumatic oil, chrysene, and a little charcoal (Boudet & Boissenot). 2. It is saponified with difficulty by boiling with *potash-ley*, more easily by alcoholic potash, or by fusion with potash hydrate, being thereby resolved into melissic alcohol and palmitic acid (Brodie). — Ettling and Boudet & Boissenot did not succeed in saponifying it.

Besides the above products, other bodies are obtained from crude myricin: *a.* In the purification of myricin by crystallisation from ether or coal-naphtha, there remains in the mother-liquor a body resembling melissic alcohol, melting at 72° to 78 5°, and containing, when it melts at 72°, 82·22 p. c. C., 14·14 H., and when melting at 78·5°, 82·59 p. c. C., 14·27 H.; its melting-point cannot be reduced below 72°. When heated with potash-lime, it yields an acid melting at 77·5°, containing 78·16 p. c. C., and 13·03 H.. and in the silver-salt 60·68 p. c. C., 10·03 H., and 22·25 Ag. — *b.* With the palmitic acid there occurs an acid of lower melting-point, difficult to separate (Brodie). — By treating myricin with potash-ley, Lewy obtained his *myriçic acid*, melting at 60·5° and containing 77·78 p. c. C., and 13·17 H., doubtless a mixture.

Myricin dissolves very slightly in *alcohol*, but with moderate facility in pure *ether* (Brodie). It requires for solution 123 parts (Buchholz & Brandes), 200 parts (John) of boiling absolute alcohol, and 99 parts of cold ether (Buchholz & Brandes). It dissolves easily in hot *oil of turpentine*, from which it does not separate on cooling (John), and more easily than cerin in cold capnomor (Reichenbach).

Appendix to Melene.

1. Bees'-wax.

Consists principally of a portion soluble in alcohol, cerin [Brodie's cerotic acid (p. 134)], and a portion nearly insoluble therein, myricin (p. 153), the two bodies being present in varying proportions.

John found a large quantity of cerin and little myricin. Buchholz & Brandes found 90 p. c. cerin, and 8 p. c. myricin; Boudet & Boissenot, 70 p. c. cerin, 30 myricin. One wax investigated by Brodie contained 22 p. c. cerotic acid, which was altogether wanting in a wax produced by wild bees in Wiltshire, and in Ceylon bees-wax. — Van der Vliet (*J. pr. Chem.* 16, 302) considered wax to be a single substance; Gerhardt (*N. Ann. Chim. Phys.* 15, 236) regarded it as the aldehyde of stearic acid.

Wax also contains a substance to which it owes colour, smell, and taste, and a resinous yellow colouring matter, which remains in solution when yellow wax is dissolved and the solution cooled (Bizio, *Brugn. Giorn.* 15, 347). — Its adhesiveness is due to an oily substance, which dissolves in alcohol, and remains in the mother-liquor after crystallising out the cerotic acid (Brodie), and when recovered by evaporation forms Lewy's *cerolein*, melting at 28·5°, easily soluble in cold alcohol and ether, and containing 78·74 p. c. C., 12·51 H., and 8·75 O. This body may be resolved into an acid and a non-saponifiable substance. — Alcoholic extracts of wax contain, besides cerotic acid, small quantities of an acid resembling margaric acid, the lead-salt of which, precipitated by neutral acetate of lead, dissolves in the alcoholic liquid on boiling, and is obtained in crystalline granules on cooling the solution (Brodie). — Crude wax yields an aromatic principle when distilled with water.

When bees-wax is exposed to air and light, it loses its colour, taste, and smell, and is converted into *white* or *bleached wax.*

This change takes place more rapidly on the addition of oil of turpentine (Ostermaier, *Repert.* 48, 97; Schmidt, *Jahrb. pr. Pharm.* 2, 211). Wax is also decolorised by treating it with ether, which dissolves the colouring matter (Hess). — Concerning the alteration which had taken place in the wax from an antique lamp, and the *Acide cerantique* obtained therefrom, see Braconnot (*N. Ann. Chim. Phys.* 21, 484).

Bleached wax is brittle in the cold; has a splintery, not crystalline fracture; is flexible when warmed; and melts at 61° to 64°. Melted wax begins to be turbid at 64°, and solidifies completely at 62·75°, with smooth surface (Chevreul). — Under certain circumstances, wax exhibits a crystalline structure under the microscope (Dujardin, *Compt. rend.* 30, 172). See also Böttger (*N. Jahrb. Pharm.* 16, 309; *Chem. Centr.* 1862, 80). — Sp. gr. 0·96 (Bostock), 0·962 (Legrip), 0·966 in the solid state, 0·834 at 81°, 0·8247 at 94°, the sp. gr. of water at 15° being 1 (Saussure). Wax adulterated with tallow is lighter, and has a lower melting-point.

	Hess.		Marchand.		Van der Vliet.		Lewy.	
	a.	*b.*	*a.*	*b.*	*a.*	*b.*	*a.*	*b.*
C	79·30	79·06	79·83	80·00	80·54	80·61	80·23	79·24
H	13·20	13·16	13·44	13·16	13·52	13·50	13·39	13·18
O	7·50	7·78	6·73	6·84	5·94	5·89	6·38	7·58
	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00

Hess treated yellow wax with ether, and examined (*a*) the undissolved, and (*b*) the dissolved portion. Marchand's analysis (*a*) was made with yellow wax, decolorised by a little ether; the analysis (*b*) with virgin wax. Van der Vliet proceeded in the same manner as Hess. Lewy analysed (*a*) crude, and (*b*) bleached wax.

Wax boils at a temperature about 20° higher than the boiling-point of spermaceti. It yields by *dry distillation*, first a watery liquid, then *wax-spirit*, then a thick distillate, partly solidifying in the neck of the retort, *wax-butter*, and lastly a thin yellow *empyreumatic oil.* During the whole of the distillation, an evolution of carbonic acid and gaseous hydrocarbons [homologous with ethylene (Gerhardt)] takes place. If the distillation be suspended before it is complete, the residue forms a black, elastic, greasy mass; when it is continued to the end, nothing remains but charcoal (John; Ettling). — When wax is gently boiled, traces only of gas and aqueous liquid, but a large quantity of solid distillation-products, are obtained; rapid distillation produces more gas and empyreumatic oil (Fromherz).

The aqueous distillate contains acetic and propionic acids (Poleck). Sebacic acid (Fromherz; Boudet & Boissenot), and acrolein are never obtained from wax (Poleck). The cerotic acid of wax, which distils unaltered *per se*, is not found in the distillate from wax (Brodie). See p. 137. Wax-butter, after pressing and melting with warm-water, is white and brittle. It is resolved by boiling with potash-ley into a fatty acid which dissolves [palmitic acid derived from the myricin (Brodie); margaric acid according to older statements], and melene, which solidifies on cooling (Ettling's paraffin, p. 150). In this decomposition it yields neither glycerin nor volatile acids (Poleck, *Ann. Pharm.* 67, 171). — By repeated distillation, the wax-butter is converted into a very limpid yellow oil, *wax-oil*, which has a very pungent taste and smell, and, when rectified, first with water and afterwards over potash, and dried, is of sp. gr. 0·7502 at 11°, boils at 137°, and contains 84·3 p. c. C., 14·3 H., and 1·4 O. It turns syrupy and carmine-red with oil of vitriol, and when treated with dry hydrochloric acid gas, becomes dark-red, and deposits red, probably crystalline drops (Ettling).

The empyreumatic oil from wax deposits laminæ of melene in the cold. When freed from adhering margaric acid by potash, and rectified, it leaves more melene; the distillate, after treatment with potassium, boils at 160° to 220° and higher, but at all points of the distillation the product contains equal numbers of atoms of carbon and hydrogen (85·4 p. c. C., 14·6 H.) (Gerhardt).

Wax mixed with spongy platinum, and heated to 100°, is completely converted into carbonic acid and water by a sufficiently prolonged current of *oxygen*; at 280° it enters into brilliant combustion (Reiset & Millon, *N. Ann. Chim. Phys.* 8, 285). — Wax is attacked by strong *nitric acid* on gentle warming, the action being at first violent, afterwards more moderate. After digesting for some days, it floats on the surface of the acid as a thick oil, but on still longer digestion, with addition of fresh acid, it dissolves completely. The solution still continues to evolve red fumes, and if boiled till the fumes disappear, it yields, on evaporation, crystals of succinic acid, giving off at the same time a small quantity of volatile oil of rancid odour (Ronalds, *Ann. Pharm.* 43, 356). Wax boiled for two hours with nitric acid is converted into a solid mass, which is soluble in carbonate of soda, and after boiling with the acid for 24 hours, is completely dissolved, with the exception of œnanthylic acid which floats on the surface. When wax is boiled with nitric acid till it is completely dissolved, the solution yields on evaporation, pimelic, adipic, and lipic acids, but no suberic acid (Gerhardt). Deschamps (*N. J. Pharm.* 4, 205) obtained suberic, succinic, and butyric acids from white and yellow wax, and from cerin and myricin, which, according to other statements, yield also oxalic and acetic acids.

Crude wax is bleached by melting it in *chlorine-water*, or in aqueous chloride of lime, but it takes up chlorine at the same time. — It forms with *oil of vitriol*, when heated, a dark-brown transparent solution, which becomes turbid and thick on cooling, and is precipitated by water.

One hundred parts of wax, saponified with 200 parts of *caustic potash* and water, yield 34·6 parts of mixed acids, and 56·7 parts of non-saponifiable substance. The latter body begins to solidify at 75°, is quite solid at 72°, but still remains soft at 64° (Chevreul). By very strong potash-ley wax is entirely converted into a soluble soap (Lewy). When wax is boiled for 6 hours with potash-ley, it is distinctly attacked, swells up, and separates from the liquid as a creamy mass, easily soluble in water (Berzelius, Warington & Francis, *J. pr. Chem.* 32, 282). With fused caustic potash it produces the *pseudo-ceraïn* of Warington & Francis, a body allied to ceraïn (p. 135), and, like it, undoubtedly a mixed substance. See also Deschamps (*N. J. Pharm.* 4, 205), who by the action of potash on wax, obtained butyric, ulmic, and margaric acids, an acid oil, and a non-saponifiable substance.—The wax-soap is very hard; the acid separated from it melts at 70° (Geiger & Oppermann, *Mag. Pharm.* 35, 62). — A little wax is saponified also by boiling for a very long time with *carbonate of soda* (*Repert.* 94, 153). — Wax forms with warm aqueous *ammonia* an emulsion which deposits it on cooling, in flocks which are more easily fusible than wax, and apparently slightly soluble in water (Bostock). — It is insoluble in a boiling aqueous solution of *borax* (Batka).

Wax may be melted together with *phosphorus*, *sulphur* and *selenium*. — It is insoluble in cold *alcohol*, but soluble, according to Bostock & Boullay, in 20 parts, and, according to Chevreul, in 50 parts of boiling alcohol of sp. gr. 0·816. Alcohol of sp. gr. 0·804 dissolves yellow and white wax completely; weaker alcohol dissolves only white wax (Van der Vliet, *J. pr. Chem.* 16, 302). — Wax is insoluble in cold, but soluble in 10 parts of boiling *ether* (Bostock). — It dissolves partially in cold *chloroform* (A. Vogel), in which yellow wax turns white (Batka). It is soluble in hot *acetone*, partially separating on cooling (Chenevix), and in all proportions of warm *volatile oils*, which deposit the greater part on cooling. Melted wax mixes with *fat oils*, forming unctuous masses, *cerates*. — On the adulteration of wax and its detection, see Chateau (*Mulhous. Soc. Bull.* 32, 406); on the detection of paraffin in wax, see Liès-Bodart (*N. J. Pharm.* (4) 3, 217).

2. Other varieties of Wax.

Wax of Leaves and Fruits.—The *wax of cabbage-leaves* is fusible, and after melting solidifies at 75° to 73° to a soft mass, hardening at 65°. It is not saponifiable by caustic potash (Chevreul). — Einhof (*A. Gehl.* 6, 63) obtained from *green barley-stalks* a green saponifiable wax, and from the dry straw a yellow wax.

When leaves (of *Pyrus communis*) which have become yellow are freed from leaf-yellow (xvi, 515) by exhausting them with cold alcohol, and afterwards boiled with alcohol, the decoction solidifies to a jelly on cooling. This jelly, when washed with cold alcohol and dissolved in boiling alcohol, is obtained in milk-white, chalky lumps, which melt at 75° and are solid and opaque after cooling. The wax is inodorous and tasteless; it distils unchanged out of contact with air, and is insoluble in caustic potash. It dissolves in 425 parts of alcohol, and is deposited from a hot solution, on cooling, in the form of a translucent paste. It is rather more freely soluble in cold ether (Berzelius, *Ann. Pharm.* 21, 258).

When *grass* is exhausted with ether, the solution evaporated and the residue dissolved in boiling alcohol, the solution deposits on cooling a white wax, containing after fusion, 79·3 p. c. C., 13·3 H., and 7·4 H. — The leaves of syringa similarly treated yield a wax containing 79·9 p. c. C., and 13·3 H., and resembling the wax of vine-leaves (Mulder, *J. pr. Chem.* 32, 174).

The *white rime with which fruit is covered* is a resin which exists as a varnish while the fruit is unripe, and appears as a white powder only on the ripe fruit. It is dissolved by washing the whole fruit with ether, and remains, on evaporating the solution, as a white, very light powder; or if the ether contains alcohol, the residue solidifies to a jelly. — The resin is amorphous, inodorous, and tasteless; it melts at about 250°, without previous softening, to a brown mass, which is friable when cold, and carbonises about 300°, giving off empyreumatic oil. It is attacked by nitric acid, when heated, and converted into a bitter substance soluble in water. Dissolves in oil of vitriol, with dark-purple colour. Not saponifiable by strong potash-ley. — Dissolves in alcohol and ether, also in volatile fat oils (Berthelot, *N. J. Pharm.* 9, 177).

The wax of fruit melts only above 200° (Baudrimont, *N. J. Pharm.* 3, 404).

Wax of Angelica root. — Obtained in the preparation of angelic acid, according to x, 413, and purified by washing it with water and crystallising from boiling alcohol. White flocks or nodules, without taste or smell, rather softer than bees'-wax, and easily fusible. Melts in boiling potash-ley, without dissolving. Dissolves more easily than bees'-wax in alcohol and ether (Buchner, *Repert.* 76, 166).

Wax of Antiar Upas. — Deposited from an extract of the juice prepared with hot alcohol on cooling, and purified by boiling with water. See xvi, 217. — White, brittle wax, softening at 30°, and melting at 35°. Sp. gr. 1·016 at 20°. — Decomposed by nitric acid; blackened by oil of vitriol; not affected by hydrochloric acid or potash-ley. Soluble in alcohol and ether, especially on boiling. — Contains on the average 77·29 p. c. C., 11·71 H., and 11 O. (Mulder, *Pogg.* 44, 414).

Radix Aristolochiæ antihystericæ contains a wax allied to cork-wax (Wittstein, *Repert.* 57, 152).

Arnica wax. — The substance formerly known by this name was found by Walz to consist of myristate of magnesia.

Wax or *resin* forming the principal part of the wood of *Balanophoræ* (a family of parasitic plants from Java). — Melts between 90° and 100°. The crude, somewhat sticky substance is rendered brittle and friable by prolonged boiling with water, whereby a trace of volatile oil is evolved. Neutral. — When purified by dissolving it twice in ether, boiling with water, and drying at 100°, it contains 79·58 p. c. C., 11·22 H., and 9·20 O., corresponding approximately with the formula $C^{12}H^{10}O$. — It emits an agreeable odour when burnt, and leaves a light combustible charcoal. It is but slightly attacked by cold fuming nitric acid, and gradually dissolves in the dilute acid on warming. It dissolves in oil of vitriol to a fine brown-red liquid, from which water precipitates it unaltered and white. It is not affected by boiling for some hours with strong potash-ley. — Dissolves very slightly in alcohol, forming a solution which is turned white by water, and not rendered clear by ammonia. Soluble in all proportions of ether (Poleck, *Ann. Pharm.* 67, 179).

¶ *Canaüba wax.* — Forms a coating on the leaves of the Canaüba tree of Brazil (*Copernicia cerifera*). Light yellow with a tinge of green, considerably harder than bees'-wax at ordinary temperatures; melts at about 84°; has a sp. gr. of 0·99907; and leaves about 0·14 p. c. ash when burnt. By saponification with alcoholic potash it yields a considerable quantity of melissic alcohol, melting at about 88° (p. 151), which exists in the wax in the free state, and may also be dissolved out from it by alcohol. — The wax also contains small quantities of other alcohols, very difficult to separate. By repeated crystallisation from benzol and ether, it appears to yield an alcohol, $C^{46}H^{48}O^2$, melting at 78°, and a substance, $C^{78}H^{82}O^{6}$, melting at 105°. — Lastly, the wax contains a mixture of several acids, differing in their melting points, but very difficult to separate from a resinous body which adheres to them (Maskelyne, *Chem. Soc.* [2], 7, 87). ¶

Carnauba wax (probably identical with the preceding). — Exists in thin films on the leaves of a Brazilian palm [*Corypha cerifera* (Virey, *J. Pharm.* 20, 112)] and falls off in scales when the leaves are dried in the shade (Sigaud, *N. J. Pharm.* 5, 154). Purified by melting. — Pale-grey powder, melting at 97°, and solidifying to a cracked, dirty-green mass of sp. gr. 0·98. Has an agreeable odour of new hay, and is nearly tasteless. It carbonises when heated in chlorine, and is turned brown by oil of vitriol, becoming less fusible and inflammable. When boiled for half an hour with potash-ley, it acquires a reddish colour, but is not dissolved or saponified (Brande, *Gilb.* 44, 287). The solutions in boiling alcohol and ether solidify on cooling, from separation of a purer wax, which is crystalline, very brittle, and friable; melts at 83·5°, and contains 80·33 p. c. C., 13·07 H., and 6·60 O. (Lewy, *N. Ann. Chim. Phys.*, 13, 449). It yields by dry distillation a product resembling paraffin, containing 85·24 p. c. C., and 14·93 H. (Lewy, *N. Ann. Chim. Phys.* 5, 395).

Coca wax. — In coca leaves. In the preparation of cocaine, according to xvi, 302, 2, this wax is precipitated by lime, and may be extracted from the washed and dried lime-precipitate by ether, together with leaf-green. The ethereal solution is evaporated; the residue is dissolved in boiling alcohol; and the granules deposited on cooling are purified by recrystallisation from boiling alcohol. — Light, white granular mass, brittle and dry to the touch, becoming electric when rubbed. Melts at 70°. Contains 80·2 p. c. C., 13·4 H., and 6·4 O., corresponding with the formula $C^{66}H^{66}O^{4}$ (calc. 80·16 p. c. C., 13·36 H.). — Carbonises when heated, evolving empyreumatic products, but no perceptible ammonia or acrolein. Dissolves in hot potash-ley. Insoluble in water and in aqueous acids and alkalis. Dissolves slightly in cold, more freely in boiling alcohol, and very easily in ether (Niemann, *Dissertation*).

Cork-wax. — Chevreul's *cerin.* — Extracted by hot alcohol from cork previously exhausted with water. The alcoholic liquid, when concentrated and cooled, deposits crystals of cerin, amounting to 1·8 to 2·5 p. c. of the cork (Chevreul). — Small, white, transparent needles, which soften and sink in boiling water (Chevreul). Pale-yellow needles, containing 74·87 p. c. C., 10·49 H., 14·64 O. (Döpping).

Cork-wax heated in a glass tube does not melt, but gives off empyreumatic products which do not smell of acrolein. On platinum foil it burns with a bright flame (Döpping). When subjected to dry distillation it yields a little acid water and a large quantity of oil, which partly solidifies in the crystalline state on cooling (Chevreul). It dissolves in hot nitric acid, evolving nitric oxide and forming oxalic acid and a product precipitable by water (Chevreul). On boiling with weaker nitric acid the products are nitric oxide, carbonic acid, a little oxalic acid, and ceric acid, which floats on the surface in the form of an oil. Very strong nitric acid acts in a similar manner, but dissolves a part of the ceric acid, which is precipitated by water (Döpping). — The wax dissolves in oil of vitriol with blackening (Döpping). When boiled with potash-ley it turns yellow or brown without dissolving.

The wax dissolves in 413 parts of boiling alcohol of sp. gr. 0·816 (Chevreul). — (Chevreul, *Ann. Chim.* 96, 170; *Schw.* 16, 331). Döpping (*Ann. Pharm.* 45, 287). See also Bley (*N. Br. Arch.* 17, 179). It is uncertain whether Boussingualt's cork-resin (xvi, 204) belongs to this place or not.

Ceric acid. Produced by the action of nitric acid on cork-wax, or by treating cerin with a little nitric acid of sp. gr. 1·35, whereupon the ceric acid rises to the surface as an oil, a part remaining in solution and being precipitated on addition of water. The product is washed with hot water, dissolved in alcohol, and evaporated. It forms a yellowish-brown, translucent, waxy mass, melting below 100° and containing 64·23 p. c. C., 8·77 H., and 27·00 O. It dissolves easily in ammonia and potash, from which it is precipitated by acids. It forms a neutral lead-salt containing 22·40 p. c. PbO., obtained by precipitating the alcoholic acid with neutral acetate of lead, and a basic salt containing 46·18 p. c. PbO., obtained by precipitating the ammoniacal acid with neutral acetate of lead (Döpping, *Ann. Pharm.* 45, 292)

Wax from the milk of the Cow-tree (*Galactodendron utile*). — When the residue left on evaporating the milk is exhausted with cold absolute alcohol and with alcohol of sp. gr. 0·89, these liquids take up resins; and from the undissolved portion, boiling absolute alcohol dissolves the wax, which it deposits on cooling. — Neutral small grains, made up of microscopic pointed needles Melts at 65° and is saponified with difficulty by potash. Dissolves sparingly in cold, more freely in boiling ether, which becomes turbid or gelatinous on cooling. Contains 78·82 p. c. C, 12·39 H., and 8·79 O., corresponding to the formula $C^{70}H^{66}O^{6}$. The same wax occurs in a vegetable milk from Marmato, in Columbia (Heintz, *Pogg.* 65, 240). See also Boussingault & Ricero (*Ann. Chim. Phys.* 23, 219), Solly (*Phil. Mag.* 11, 452). The wax of the cow tree is identical with bees'-wax (Boussingault, *Ann. Chim. Phys.* 59, 24).

The ripe *capsules of the blue-seeded poppy* contain a wax sparingly soluble in ether, allied to ceraïn, and an easily soluble wax allied to myricin (Winckler, *Repert.* 59, 27).

Cuba wax. — Dirty yellowish-brown, or liver-coloured wax, honey-yellow in thin sheets, rather softer than ordinary bees'-wax. It is insoluble in water, but completely soluble in boiling alcohol, hot oil of turpentine, and boiling ether. In cold ether it falls to a granular powder. Contains 9 p. c. of soft resin, 77 p. c. of cerin, and 10·5 p. c. of myricin (Brandes, *Ann. Pharm.* 10, 239).

Wax of Elecampane root. — Obtained by exhausting the root, first with water, then with boiling alcohol, which deposits the wax on cooling. — Yellowish-white, tough between the teeth, and somewhat sticky. Tasteless. Deposited from its solution in hot alcohol and ether in the form of a yellowish-white powder (John, *Chem. Schrift.* 4, 65). Probably impure helenin (xvii, 522).

Wax of Hops. — Extracted from fresh hops by ether, together with hop-bitter and other substances, and purified by treating the ethereal extract with cold alcohol, which leaves it undissolved, and crystallising from hot alcohol (Lermer, *Pharm. Viertelj.* 12, 506).

Wax of Juniper berries. — When the berries are boiled with alcohol and the decoction is filtered hot, it deposits on cooling a grey, brittle, friable wax, which melts to an oil in boiling water, emitting an odour of wax. When submitted to dry distillation, or when burnt, it behaves like other waxes. It is converted into a resin by long boiling with nitric acid, and does not dissolve in aqueous potash, even after prolonged boiling. It is freely soluble in hot alcohol, which deposits the whole of it on cooling; insoluble in cold, but soluble in hot ether; and easily soluble in warm fatty and volatile oils (Trommsdorff, *Taschenb.* 1822, 48). Nicolet's juniper wax (*J. Pharm.* 17, 312), extracted by alcohol from juniper berries, previously boiled with water and dried, behaves in a similar manner. — When juniper berries are distilled with water to obtain the volatile oil, the residue in the still, strained while hot, deposits on cooling and concentrating, a mixture of wax and resin, from which cold alcohol takes up the resin. The undissolved wax, purified by repeated crystallisation from alcohol, with the help of animal charcoal, is white and fusible, and breaks up, after fusion, into hard angular pieces, which are translucent and lustrous. It dissolves in boiling potash-ley, and is deposited on cooling (Steer, *Wien. Acad. Ber.* 21, 383).

The pollen of *Lilium croceum* gives up to ether a yellow wax, which bleaches on exposure to light, and is saponified with difficulty by potash. It contains 79·59 p. c. C., 12·04 H., and 8·37 O. (Frémy & Cloez, *N. J. Pharm.* 25, 161; *Pharm. Centr.* 1854, 458).

Wax of the fruit of the Mountain Ash and of the root of the Apple-tree. — *a.* Extracted from the fruit by ether and bleached by chlorine. — *b.* Obtained in the preparation of phloridzin. According to Mulder, both waxes have the same composition, and occur generally throughout the vegetable kingdom; *a* contains 68·49 p. c. C., and 9·27 H.; *b*, 68·69 p. c. C., and 8·88 H. (Mulder, *J. pr. Chem.* 32, 172).

Palm-wax. — *Ceroxylin* or *Cerosilin.* — The trunk of *Ceroxylon Andicola*, a palm of New Granada, is covered with a substance which may be scraped off, and when purified by boiling with water and made into balls, forms the *cera de palma.* It is a mixture of wax and resin (xvii, 405), from which the wax may be separated by dissolving it in a large quantity of boiling alcohol: the solution deposits the wax, on cooling, in the form of a white jelly, which is freed from adhering resin by crystallising it repeatedly from boiling alcohol. — Very delicate silky needles (Bonastre). Yellowish-white, resembling bees'-wax, melting in boiling water (Boussingault), at 72° (Lewy), to a faintly coloured liquid. Contains, on the average, 80·3 p. c. C., 12·7 H. (Boussingault), 80·7 p. c. C., 13·3 H. (Lewy). Dissolves in boiling alcohol, and more freely in ether. Boussingault (*Ann. Chim. Phys.* 29, 333; 59, 19). Lewy (*N. Ann. Chim. Phys.* 13, 447). Bonastre (*J. Pharm.* 14, 349). The wax known as *Cire des Andaquies* contains, besides cerosin (p. 61), a substance resembling palm-wax, which dissolves less easily than cerosin in boiling alcohol, melts at 72°, and contains 80·95 p. c. C., 13·37 H., and 5·68 O. (Lewy). — The wax dissolved off the leaves of *Chamærops humilis* is resolved by boiling alcohol into cerin and myricin. The leaves also give up cerin to boiling alcohol (Teschemacher, *Phil. Mag.* 28, 350; *J. pr. Chem.* 39, 220).

Wax (?) from the bark of Platanus acerifolia. — Obtained by boiling the ethereal extract of the bark with dilute potash-ley to remove colouring matter, dissolving the residual powder in ether, and evaporating.—Yellowish-white, amorphous powder, without taste or smell. Melts to a yellow oil at about 180°, and burns with a smoky flame, emitting an aromatic odour. When subjected to dry distillation, it yields a yellow oil, leaving a large quantity of charcoal. It is insoluble in water and not saponifiable by potash; dissolves with difficulty in hot aqueous ammonia, and is almost entirely deposited on cooling, as a jelly. Contains on the average, 79·64 p. c. C., 11·01 H., and 9·35 O. (Stähelin & Hofstetter, *Ann. Pharm.* 51, 74).

Wax of Black Poplar buds. (Pellerin, *J. Pharm.* 8, 432.)

The ripe *capsules of the blue-seeded poppy* contain a wax sparingly soluble in ether, and allied to cerain, and an easily soluble wax allied to myricin (Winckler, *Repert.* 59, 27).

Propolin.—Obtained by exhausting propolis (the substance with which bees fill up crevices in their hives) with boiling alcohol and cooling, whereby resinous substances are retained in solution.—Melts at 57° to 58°, emitting an odour of honey (Pellerin, *J. Pharm.* 8, 433). See Debeauvoys (*Compt. rend.* 26, 116).

Propolis is a blackish substance, translucent at the edges, soft at first, but becoming harder in time. It contains, according to Vauquelin, 14 p. c. of wax, 57 of resin, and 29 of acid and foreign admixtures. The resin is greenish-brown, translucent, and brittle (Vauquelin, *Ann. Chim.* 42, 265). The acid appears to be a mixture of gallic and benzoic acids (Cadet, *Bull. Pharm.* 1, 72).

Wax obtained from Rye-starch by the action of nitric acid.—When rye-starch is employed for the preparation of saccharic acid, there floats on the surface of the acid liquid a wax which dissolves in alcohol and more freely in ether, and forms with alkalis a compound soluble in water and decomposible by acids. It contains 72·38 p. c. C., 12·14 H., and 14·48 O. (Hess, *J. pr. Chem.*, 13, 411).

Wax of Shellac.—Extracted from seed-lac by alcohol. Dirty-white powder, insoluble in cold alcohol. The solution in hot alcohol solidifies to a jelly on cooling (John, *Chem. Schrift.* 5, 18). It distils unchanged in a vacuum, and dissolves to a very slight extent in strong potash-ley, from which it is precipitated by acids unaltered (Berzelius, *Pogg.* 10, 256). Shellac contains 3 per cent. of a hard, yellowish-white wax, resembling Japan wax (Buchner, *Ann. Pharm.* 59, 100).—A solution of a *spurious shellac* in boiling alcohol deposited light white scales of a friable wax, melting at 60°, saponifiable by boiling potash-ley, and slightly soluble in cold ether, cold rock-oil, and oil of almonds (Nees v. Esenbeck & Marquart, *Ann. Pharm.* 13, 288).

Wax of raw Silk.—Exists in raw silk to the extent of 1 part in 200 to 300. Faintly coloured, solid, and brittle. Soluble in alkalis and soap-water. Dissolves in 2,000 parts of cold, and in 300 to 400 parts of boiling alcohol of sp. gr. 0 829: on cooling the solution first deposits flocks and then solidifies to a paste (Roard, *Ann. Chim.* 65, 63).—The wax deposited from the alcoholic tincture of white or yellow silk is grey, fusible, and combustible. It is decomposed by warm oil of vitriol, but not by strong nitric acid. It is partially soluble in boiling potash-ley, which deposits part of the dissolved portion on cooling; is soluble in glacial acetic acid, alcohol, ether, and fatty and volatile oils (Mulder, *Pogg.* 37, 609). This wax does not smell of acrolein when burnt, and is not acid in alcoholic solution. When its solution is precipitated with basic acetate of lead, the precipitate decomposed under ether by hydrosulphuric acid, and the ether evaporated, there remains a wax melting at 48°. The original wax is, moreover, only partially saponifiable by alcoholic potash; when it is melted with caustic potash, hydrochloric acid throws down from the product a fatty acid melting at about 80° (Cramer).

Wax of Sumach.—Extracted by chloroform from the leaves of *Rhus coriaria.* Resembles Japan wax, but smells of violets. When boiled with an aqueous solution of borax, it forms a soap, which solidifies to a jelly on cooling, and is precipitated by acids (Batka, *Chem. Centr.* 1865, 12).

Wax (?) from Sumatra (Getah Lahoe).—According to Blaine, the inspissated sap of *Ficus cerifera.* Ash-grey, harder and more brittle than bees'-wax; sp. gr. 0·936 at 16°. It becomes sticky in warm water and melts to a clear liquid at 61°, giving off water and depositing a black powder: on cooling it solidifies to a waxy mass. According to Bleckrode it melts to a syrup at 50° and to a limpid liquid at 75°. Burns from a wick with a bright smoky flame. Insoluble in weak spirit, but gives up about 10 p. c. of a sticky substance to absolute alcohol; dissolves in ether, with the exception of about 1 p. c., also in oil of turpentine and rock-oil, but not in bisulphide of carbon, in which it turns white and flocculent (Kaiser, *Chem. Centr.* 1856, 477; *Kopp's Jahresber.* 1856, 632). It is bleached by boiling potash-ley, without dissolving therein. When submitted to dry distillation, it yields crystals melting at 37·5°. Dissolves in boiling alcohol, forming a brown solution, which, on cooling, deposits a white crystalline powder, melting at 55° (Bleckrode, *N. Jahrb. Pharm.* 7, 182; *Kopp's Jahresber.* 1856, 633).

Wax from Thuja occidentalis.—Deposited from the alcoholic decoction of the green part of thuja on cooling. The mother-liquor may be made to yield a further quantity by concentrating and mixing it with water, dissolving the precipitate thereby produced in boiling alcohol, precipitating with neutral acetate of lead, and decomposing this precipitate with hydrosulphuric acid.

			Kavalier.
32 C	192	75·00	74·91
32 H	32	12·50	12·44
4 O	32	12·50	12·65
$C^{32}H^{32}O^4$	256	100·00	100·00

Has the same composition as palmitic acid, and a wax from the exfoliating bark of *Pinus sylvestris* (p. 16).

Decompositions. 1. By prolonged boiling with potash-ley, the wax yields a soap which cannot be filtered. It is precipitable by chloride of sodium and chloride of calcium, but a portion remains in solution and may be thrown down from the filtrate by hydrochloric acid, and further decomposed by alcohol. The lime-soap gives up to ether the wax *a*, which may be resolved by alcohol into two portions of unequal solubility. From the rest of the lime-soap hydrochloric acid throws down the acid *b*, which crystallises in cauliflower-like crystals.

	Wax a.	Kawalier.
58 C	79·45	79·40
58 H	13·24	13 17
4 O	7 31	7·43
$C^{58}H^{58}O^{4}$	100 00	100·00

	Acid b.	Kawalier.
58 C	70·44	70·19
58 H	11 74	12·02
11 O	17·82	17 79
$C^{58}H^{58}O^{11}$	100 00	100·00

The acid *b* forms a baryta-salt containing 54·20 p. c. C., 9·04 H., 12·45 O., and 24·31 BaO., corresponding to the formula $C^{58}H^{57}O^{10},2BaO$ (Kawalier).

2. Thuja wax heated with soda-lime to 250° gives off water and an oily body: the residue treated with water, ether, and hydrochloric acid in succession, gives up to water a salt from which hydrochloric acid precipitates the *acid c;* to ether the white brittle wax *d;* the hydrochloric acid throws down from the rest of the lime-soap, the acid *e*.

	Acid c.	Kawalier.
36 C	68 35	68·19
36 H	11 39	11·10
8 O	20·26	20 71
$C^{36}H^{36}O^{8}$	100·00	100 00

	Wax d.	Kawalier.
36 C	80·0	79 85
38 H	14·1	14·01
2 O	5·9	6 14
$C^{36}H^{38}O^{2}$	100·0	100·00

	Acid e.	Kawalier.
36 C	72 48	72·41
34 H	11·41	11·88
6 O	16·11	15·71
O^{6}	100 00	100 00

Thuja wax otherwise prepared yielded a wax containing 80·75 p. c. C.; the lime-salt, insoluble in ether, yielded the *acid f*, from which the corresponding baryta-salt was obtained (Kawalier, *Wien. Acad. Ber.* 13, 514).

	Acid f.	Kawalier.
58 C	70·31	70·06
58 H	11·91	11·95
11 O	17·78	17 99
$C^{58}H^{58}O^{11}$	100·00	100·00

	Baryta-salt.	Kawalier.
58 C	53 78	53·69
58 H	8·96	9·02
11 O	13·61	13·18
2 BaO	23·65	23·48
$C^{58}H^{58}O^{11}$ + BaO	100·00	100·00

Wax of Tormentil-root. — Meissner (*Berl. Jahrb.* 29, 2, 63).

3. Paraffin.

Reichenbach (1830). *Schw.* 59, 436; 61, 273; 65, 295. — *J. pr. Chem.* 1, 379; 73, 111.
J. Gay-Lussac. *Pogg.* 24, 180.
Schrötter. *Pogg.* 59, 39.
Hofstätter. *Wien. Acad. Ber.* 13, 436; *Ann. Pharm.* 91, 326.

From *parum affinis.* — Discovered and investigated by Reichenbach.

In the dry distillation of many organic substances and fossil products, solid waxy bodies are obtained, which are distinguished by the general name paraffin. These bodies, some of which are prepared on the manufacturing scale, differ from one another, and from

Reichenbach's paraffin, in melting point, and in their behaviour towards oil of vitriol and solvents. They may be regarded either as imperfectly purified paraffin, in accordance with Reichenbach's view, or, which is more probable, as (like Reichenbach's paraffin) members of a homologous series, mixed or isolated hydrocarbons of the formula C^nH^n, or C^nH^{n+2}. Oxygenated products have also been confounded with paraffin. Previous to Reichenbach's discovery, paraffin-like bodies were observed by Fuchs & Buchner (*Repert.* 9, 290) in petroleum from Lake Tegern; by L. Gmelin (*Handbuch,* 3 Aufl. 2, 511) in wood-vinegar; and by Unverdorben in rock-oil (*Schw.* 57, 244).

a. Reichenbach's Paraffin.

Source and Formation. Paraffin occurs abundantly in wood-tar, especially in that of the red beech and of thick-barked woods in general; in smaller quantity in the tar of animal substances; and in smallest quantity in coal-tar. It exists also in soot, abundantly in rapidly distilled rape-oil, and in small quantity in rock-oil (Reichenbach).—In wood-vinegar; if the empyreumatic oil which first passes over in the rectification of wood-vinegar from beech-wood be collected and re-distilled, it yields, as the residue begins to dry, a small quantity of a white sublimate, which, when recrystallised from alcohol, melts at 40 5°, and behaves like paraffin towards oil of vitriol, potash-ley, and alcohol (Gmelin).

Preparation. Tar is subjected to repeated fractional distillation, and the portions passing over last, which are richest in paraffin, are collected apart and mixed with $\frac{1}{4}$ to $\frac{1}{2}$ their volume of ordinary or fuming oil of vitriol, in portions of $\frac{1}{10}$th at a time, and shaken. The mixture becomes hot, and is to be further heated, if necessary, till the temperature reaches 100°, after which it is kept for half a day or longer at 50°, and the paraffin, which floats on the surface as an oil, is separated and washed with water. If not quite colourless, it is again treated with fresh oil of vitriol. It is now cooled, pressed between blotting-paper, crystallised from boiling alcohol, washed with weak spirit, and melted in water.—Or the paraffin obtained by cooling the distillate and filtering is distilled with 2 or 3 parts of fuming sulphuric acid, whereupon it passes over colourless.—When oil containing paraffin is mixed with an equal quantity of alcohol of 36° B., and 6 or 8 times the volume of alcohol is gradually added, the liquid becomes turbid, and deposits a large quantity of flakes, which combine to form a thick mass. This mass when washed repeatedly with alcohol of 36°, and purified by dissolving it in hot alcohol, yields paraffin.

Properties. Delicate white needles and laminæ, without taste or smell. Neutral. Under a magnifying power of 500 diameters delicate rounded laminæ, needles, and apparently five-sided granules may be distinguished. Flexible, somewhat unctuous to the touch, not greasy. It does not stain paper in the cold, but when melted it produces a greasy spot, which disappears when the paper is strongly heated several times. It is a non-conductor of electricity. Melts to a clear colourless oil at 43·75°, and on cooling solidifies to a translucent mass, having a granular fracture. Fritzsche found paraffin from wood-tar to melt at 42°; Reichenbach's paraffin was found by Bolley to melt at 43·5°, by Hofstätter at 47·5°; by recrystallisation it yielded products melting at 45°, 46°, and 48° (Hofstätter). Sp. gr. 0·87 (Reichenbach); 0·862 (Hofstätter). Boils at a high temperature and distils unchanged.

			Gay-Lussac.	Schrötter.			
40 C	240	85·71	84·06	85·22	40 C	240	85·11
40 H	40	14·29	14·99	14·86	42 H	42	14·89
$C^{40}H^{40}$	280	100·00	99·05	100·08	$C^{40}H^{42}$	282	100·00

Gay-Lussac regarded paraffin as a compound of equal numbers of atoms of carbon and hydrogen. The correctness of this view, which was at one time thought to be established, has been doubted by Anderson and others. See below.

Decompositions. Paraffin heated in a platinum spoon burns with a bright white flame free from smoke: from a wick it burns like wax. — It is not altered by heating with *peroxide of manganese* or *peroxide of lead.* — It is not affected by exposure to *chlorine* for some hours in the cold, nor by boiling strong *nitric acid,* boiling *hydrochloric acid,* or hydrochloric acid gas (Reichenbach). On boiling it with a large quantity of strong nitric acid for several days, till the liquid is no longer rendered turbid by water, succinic acid, butyric and valerianic acids, and a small quantity of a yellow nitro-compound of penetrating odour, are produced (Hofstätter). — Paraffin is not decomposed by *oil of vitriol* or fuming sulphuric acid, even after prolonged treatment at 100° (Reichenbach). — According to Gay-Lussac, oil of vitriol blackens paraffin and slowly decomposes it, with liberation of sulphurous acid: with the anhydrous acid, paraffin becomes very hot and is converted into a black mass, which does not contain sulphovinic acid. — *Fused caustic potash* and *potassium* do not act upon paraffin.

Paraffin is insoluble in *water*, *ammonia* and aqueous *alkalis* (Reichenbach), and in liquid *carbonic acid* (Gore). — Melted paraffin dissolves a small quantity of *phosphorus* and is afterwards luminous in the dark. — It does not mix with melted *sulphur*, and dissolves only a small quantity of *selenium* (Reichenbach). According to Brion (*Comp. rend.* 56, 876; *Krit. Zeitschr.* 7, 384) paraffin (commercial?) is attacked by sulphur below its melting point, but yields no crystalline products.

Absolute *alcohol* dissolves a small quantity of paraffin in the cold: 100 parts of the boiling liquid dissolve 3·45 parts of paraffin, the greater part of which crystallises on cooling, whilst that remaining in solution may be precipitated in white flocks by water. The solvent power of alcohol decreases rapidly with the strength, 100 parts of 80 p. c. alcohol at 20° dissolving only 0·33 parts of paraffin. — *Ether* dissolves paraffin rapidly and abundantly: 100 parts of ether at 25° take up 140 parts of paraffin, the whole solidifying to a white crystalline mass on slight cooling (Reichenbach). Fritzsche found wood-tar paraffin much more easily soluble in cold ether than paraffin from ozocerite.

Paraffin dissolves easily in cold *rock-oil*, *tar-oil*, and *oil of turpentine*, even in the cold. It does not mix with either *camphor* or *naphthalene* in the fused state. — Dissolves slowly in cold, and more rapidly in warm *olive oil* and *oil of almonds*. Mixes with melted *stearin*, *spermaceti* and *bees'-wax*, and forms homogeneous masses with these substances on cooling, but when melted with *tallow* or *hog's lard* it separates from the mixture in crystals as it cools. — Equal parts of paraffin and *colophony* melted together solidify to a yellow, waxy mass. — Paraffin does not mix with melted *benzoin* or black *pitch* (Reichenbach).

On the solubility of (commercial) paraffin in bisulphide of carbon, chloroform, and benzol, see A. Vorel (*Dingl.* 164, 221); in ether, Spes (*Pharm. Viertelj.* 7, 383; 9, 283); on the separation of paraffin from wax, see Liès-Bodart (*Compt. rend.* 62, 749).

b. Paraffin from other Sources.

The products obtained by the dry distillation of *peat* are rich in paraffin (Reece, *Kopp's Jahresber.* 1849, 711). This paraffin melts at 46·7°, and contains 85·10 p. c. C., and 15·11 H. (Anderson). On the manufacture of paraffin from this material, see Breitenlohner (*Polyt. Notizbl.* 1864, 879; *Chem. Centr.* 1864, 1025). — According to Simon *lignite-tar* contains paraffin (*Pogg.* 35, 160), but the products obtained by the dry distillation of the lignite of the Weissenfels appear to contain oxygen.

Boghead coal likewise yields paraffin, and also contains it ready-formed. That obtained by distillation either melts at 45·5° and is highly crystalline after cooling; or it melts at 52° and cools to a granular mass resembling white wax. The crystalline variety contains 85·11 p. c. C., and 15·22 H.; the granular 85·14 p c. C., and 15·37 H., so that both varieties (like those obtained from peat and from lignite) may probably be represented by the general formula C^nH^{n+2}, perhaps by $C^{40}H^{42}$ (calc. 85·10 p. c. C., 14 90 H.) (Anderson, *J. pr. Chem.* 72, 379). — Boghead coal, treated with alcohol and ether in succession, gives up to the latter liquid a solid body, which, when purified with charcoal and boiled with soda-ley, melts at 41° and contains 86·33 p. c. C., and 13·22 H. (Bolley & Merz, *Ann. Pharm.* 115, 61).

The product obtained by dry distillation of *bituminous shales*, when distilled with superheated steam, yields a limpid and a thick oil in succession, followed by a buttery mass. The latter oil contains paraffin, which is deposited on cooling, and after filtering and pressing, may be purified by melting; crystallising it out at a low temperature; expressing the fluid portion; heating first to 205° and afterwards to the boiling-point, with addition of 5 to 10 p. c. of oil of vitriol; separating the melted paraffin from the carbonized mass; and washing it with water or weak solution of carbonate of soda (W. Brown, *Chem. Gaz.* 1853, 476; *Kopp's Jahresber.* 1853, 766). Paraffin may also be purified by mixing it with bisulphide of carbon and pressing, or by melting it with $\frac{1}{10}$th of animal charcoal for two or three hours and filtering (Mitschel, *Chem. Centr.* 1859, 571). It cannot, however, be purified by melting it with chloride of lime, as Kletzinsky (*Polyt. Notizbl.* 19, 349) proposes, since chlorinated products are thereby formed (Dullo, *Polyt. Notizbl.* 20, 192).

Paraffin obtained from the bituminous shale of Autun, and melting at 33°, contained 84·60 p. c. C., and 14·22 H. (Laurent, *Ann. Chim. Phys.* 54, 392; *J. pr. Chem.* 2, 121). Paraffin obtained from similar material at Glasgow melted at 55°, had a sp. gr. of 0·861 at 15°, crystallised in laminæ, needles, and granules, like Reichenbach's paraffin, and behaved in the same way towards nitric acid. By fractional crystallisation it yielded products melting at 45° to 58°, all having the same composition (that melting at 45° containing 85·47 p. c. C., and 14·29 H.; that at 58°, 85·69 p. c. C., 14·29 H.) (Fillipuzzi, *Wien. Acad. Ber.* 17, 425; *J. pr. Chem.* 68, 60). The bituminous shale of Bonn yields a paraffin which when purified melts at 50·5° (Bolley). Hofstätter found the purified product to melt at 55°; by fractional crystallisation he separated portions melting at 57° to 61°, the latter containing 86·16 p. c. C., and 14·36 H.

It is with this paraffin from Bonn that Bolley's experiments on the action of chlorine appear to have been made. When chlorine is passed through melted paraffin, hydrochloric acid gas is evolved, and the mass no longer solidifies at ordinary temperatures. On continuing the current of chlorine, the melted paraffin becomes viscid, even at 100°, and after cooling is amorphous, and does not crystallise from solution. It is soluble in alcohol and benzol, but cannot be obtained free from hydrochloric acid, which it continues to evolve, even after remaining for days in the water-bath. The transparent resinous products contain, after the more or less prolonged action of chlorine:

C	34 50	39·37	55 20
H	4·19	5·30	8 26
Cl	61 42	54·80	36·29
	100·11	99 47	99·75

corresponding approximately to the formulæ $C^{10}H^7Cl^3$, $C^{10}H^8Cl^2$, $C^{10}H^9Cl$ (Bolley, *Ann. Pharm.* 106, 230).

Lewy's (*N. Ann. Chim. Phys.* 5, 359) paraffin is obtained partly from the bituminous shale of Autun, partly from wax (p. 150). That from the former source contains 84·95 to 85·22 p. c. C., and 14·76 to 14·80 H. Melting point (of which paraffin?) 46·8°; sp. gr. 0·89; boiling point 370° to 380°. Vapour-density 10 to 11·8°, but not determinable with accuracy, on account of decomposition. From these data Gerhardt (*Rev. scient.* 19, 8) deduces the formula $C^{48}H^{50}$.

Most, if not all, *earth-oil* or *petroleum* contains paraffin, as that from Lake Tegern (Fuchs & Buchner); the rock-oil of commerce, which deposits paraffin when cooled to – 6° to – 12° (Stiekel, *Jahrb. pr. Pharm.* 4, 14); the oil from Sehnde (in Hanover); from Amiano (Pelletier & Walter, *J. Pharm.* 26, 353). Pelouze & Cahours, having found in American petroleum the liquid hydrocarbons of the homologous series, C^nH^{n+2}, have been led to regard the paraffins as higher members of the same series (*Ann. Chim. Phys.* (4) 1, 5). — The paraffin from the earth-oil of Lake Tegern melts at 51° to 55°, is of sp. gr. 0·914 at 20°, and according to Buchner, jun., contains 85·22 p. c. C., and 14·83 H. It turns brown with oil of vitriol when heated above 100°, and dissolves sulphur to a brown liquid, differing therein from Reichenbach's paraffin (Kobell, *J. pr. Chem.* 8, 305).

The thick rock-oil from Rangoon, in Burmah, *Rangoon naphtha*, contains paraffin of sp. gr. 0·915, melting at 55° (Christison & Gregory, *J. pr. Chem.* 4, 1; *J. Pharm.* 21, 536). This paraffin melts at 61°, and contains 85·15 p. c. C., and 15·29 H. (Anderson). It yields by fractional crystallisation two or more hydrocarbons of the formula C^nH^n, or C^nH^{n+2} (Warren de la Rue & Müller, *Chem. Gaz.* 1856, 375; *J. Pr. Chem.* 70, 300).

The soft brown *earth-wax from Baku*, melting at 79°, of sp. gr. 0·903, yields by dry distillation 13·82 p. c. of water and gaseous products, 4·36 of carbon, and 81·82 of paraffin, which when purified melts at 54°, and contains 85·44 p. c. C., and 14·78 H. (Petersen, *Ann. Pharm.* 118, 82). See below.

On the paraffin of bees'-wax and Carnauba wax, see those substances: on that of ozocerite and neftgil see below.

¶ Paraffin from Price's factory was found by Gill & Meusel (*Chem. Soc. J.* [2] vi, 466) to melt at 56°, and after repeated crystallisation from bisulphide of carbon, at 60°. It was not converted into sulphoacid either by fuming sulphuric acid, by ordinary oil of vitriol, or by sulphuric acid diluted with one-third of its volume of water. It did not unite with hydrochloric acid when heated with it, either in the gaseous state or in aqueous solution; neither did it unite with hypochlorous acid. *Bromine* acts upon it when aided either by heat or by sunshine, half the bromine being converted into hydrobromic acid, while the other half forms a substitution-product. These reactions show that paraffin belongs to the series C^nH^{n+2}, not to the olefine series C^nH^n. The same paraffin oxidised with *chromic acid*, is converted into cerotic acid (p. 135), together with several lower acids of the same series, some solid, others liquid and volatile, amongst which acetic acid predominates. — Oxidised with 5 or 6 times its volume of *nitric acid* of sp. gr. 1·3 diluted with 1½ vol. water, it likewise yields cerotic acid, together with many other acids, among which are acetic, butyric, valeric, œnanthylic, and hydrocyanic acids, together with succinic and anchoic acids. Nitric acid diluted with 4 vols. water acts very slowly on it, forming in 12 days a small quantity of a fatty acid melting at 73°. ¶

Composition of Paraffin.

Calculations.

40 C	240	85·71	40 C	240	85·11
40 H	40	14·29	42 H	42	14·89
$C^{40}H^{40}$	280	100·00	$C^{40}H^{42}$	282	100·00
42 C	252	85·13	48 C	288	85·21
44 H	44	14·87	50 H	50	14·79
$C^{42}H^{44}$	296	100·00	$C^{48}H^{50}$	338	100·00

Analyses.

	Beech-wood Tar.		*Peat.*	*Boghead coal.*	
	Gay-Lussac.	Schrötter.	Anderson.	Anderson.	
C	84·06	85·22	85·10	85·11	85·14
H	14·99	14·86	15·11	15·22	15·37
	99·15	100·08	100·21	100·33	100·51

Bituminous shales.

	Fillipuzzi.		Hofstatter.	Lewy.	
C	85·47	85·69	86·16	84·95	85·22
H	14·29	14·29	14·36	14·76	14·80
	99·76	99·98	100·52	99·71	100·02

	Lake Tegern.	*Rangoon.*	*Baku.*	*Ozocerite.*		*Ozocerite.*	
	Buchner.	Anderson.	Petersen.	Hofstatter.		Malaguti.	Walter.
C	85·22	85·15	85·44	84·94	85·78	84·66	84·62
H	14·83	15·29	14·78	14·87	14·29	14·28	14·28
	100·05	100·44	100·22	99·81	100·07	98·94	98·90

Ozocerite.

GLOCKER. *Schw.* 69, 215.
SCHRÖTTER. *Baumgartner's Zeitschr.* 4, 173.
ERNST SCHMID. *N. Br. Arch.* 14, 208.

Magnus. *Ann. Chim. Phys.* 55, 217.
Malaguti. *Ann Chim. Phys.* 63, 390; *J. pr. Chem.* 11, 136; *Ann. Pharm.* 23, 286.
Ph. Walter. *Ann. Chim. Phys.* 75, 214; *J. pr. Chem.* 22, 181.

Bergwachs.—Amorphous compact masses, containing hydrocarbons differing in melting point, but of the same composition, and yielding by dry distillation chiefly paraffin or a very similar substance.

Ozocerite from Slanik in Moldavia is leek-green or yellowish-brown, translucent to semi-transparent, flexible, and of the consistence of tallow or wax. Sp. gr. 0·955 to 0·97. Burns with a bright flame (Glocker). Melting-point 82° (Magnus). Boils at about 210°, and yields a distillate consisting of first a little oil, then a solid mass, giving off gaseous products, and leaving 5·7 p. c. of charcoal. It is only slightly soluble in boiling absolute alcohol, but dissolves completely in bisulphide of carbon, ether, rock-oil, and oil of turpentine, forming solutions which are leek-green by reflected, and reddish-brown by transmitted light (Schrötter). Boiling ether and absolute alcohol take up little, but hot oil of turpentine dissolves it entirely (Magnus). On drenching it with ether, a portion dissolves, the rest splitting into fine spangles. Under benzol, ozocerite becomes covered with a jelly, and does not dissolve completely until it is warmed (Fritzsche).

Ozocerite from Zietrisika in Moldavia melts at 84° and boils at 300°. Sp. gr. 0·946 at 20·5°. It is not attacked by alkalis, but softens in a stream of chlorine, and becomes soluble in boiling ether. It is not affected by cold oil of vitriol, but is carbonised by hot oil of vitriol, forming with the latter a solution from which water throws down black flocks, which give up to boiling ether white crystals melting at 72° (Malaguti).

The ozocerite of Trascowiec, in Gallicia, was found by Walter to melt at 59°, and by Schmid at 65°. It is not affected by oil of vitriol; yields paraffin on distillation (Walter).

Ozocerite from Boryslaw, in Gallicia, is of a dark black-brown colour, and may be kneaded between the fingers. Its melting point is 60°; its sp. gr. 0·944. Its solution in boiling alcohol deposits, on cooling, crystals of the three forms in which paraffin crystallises. By fractional crystallisation it yields products melting at 60° to 65°, of the same composition as paraffin, and behaving in the same way with nitric acid: that melting at 61° contains 84·94 p. c. C., 14·87 H.; that melting at 65·5 85·78 p. c. C., 14·29 H. (Hofstätter).

The ozocerite from the Urpeth coal-mine near Newcastle is soft, unctuous, and sticky. It melts at 60° and becomes perfectly limpid at 70°. Contains 85·18 p. c. C. and 14·06 H., but is a mixture of at least three substances of the same composition and equally indifferent towards boiling acids. Cold ether takes up $\frac{4}{5}$ths of the ozocerite, forming a greenish-brown solution, which when allowed to evaporate, spontaneously, deposits it in brown flocks melting at 39° and of sp. gr. 0·885. From the remaining $\frac{1}{5}$th, boiling ether or alcohol takes up a colourless or pale-yellow mass of the hardness of wax and melting at 58°. The undissolved portion, amounting to $\frac{1}{6}$th of the whole, is dark-brown, soft, of sp. gr. 0·965, melts at 73°, boils at 260°, and is nearly insoluble in boiling alcohol and ether (Johnston, *Phil. Mag.* 12, 12, 389; *J. pr. Chem.* 14, 226).

When the ozocerite from Slanik is triturated and boiled repeatedly with 200 parts of alcohol of sp. gr. 0·814, the portions first dissolved melt at 75° and 78°, and are of sp. gr. 0·845 and 0·852 at 20°. After boiling fourteen times the portion dissolved has the same melting point as the brown inodorous residue, namely, 90°; its sp. gr. is 0·957 at 17·5°, and its boiling point 300°. The residue contains 84·67 p. c. C., and 14·12 H., and has, therefore, the same composition as the original ozocerite (Malaguti).

Analyses of Ozocerite.

			Moldavia.		Zietrisika.	Newcastle.
			Schrötter.	Magnus.	Malaguti.	Johnston.
C	6	85·71	84·43	84·61	85·03	85·18
H	1	14·29	13·69	15·15	13·71	14·06
CH	7	100·00	98·12	99·76	98·74	99·24

Ozocerite from Boryslaw, when melted at a high temperature, and thereby altered, is softer than the natural substance, plastic between the fingers, lighter than water, and melts at 63°. When it is digested with benzol (or with rock-oil or ether) a part only dissolves, the rest being converted into a jelly, which forms a thick homogeneous mass on warming and again solidifies to a jelly as it cools, even after the addition of sufficient benzol to dissolve it completely. The washed and dried jelly is brown-black. — The solid product obtained by the dry distillation of melted ozocerite crystallizes from boiling alcohol in laminæ, which are distinguished from wood-tar paraffin by their high melting point (62°), and by the circumstance that they dissolve very slightly in cold ether, and form with boiling ether a solution which solidifies to a jelly on cooling (Fritzsche, *J. pr. Chem.* 73, 321; *Chem. Centr.* 1858, 506).

Ozocerite submitted to *dry distillation* yields gaseous products, an oil which solidifies in the cold, and a solid distillate, leaving 3 per cent. of charcoal. The solid portion, purified by repeatedly distilling and treating it with ether till the melting point remains constant, forms Malaguti's *cire de l'ozokerit*, a substance closely resembling paraffin, and according to Hermann, identical with his *keron*. It is colourless, nacreous, of sp. gr. 0·904 at 17°, melts at 56° to 57°, is slightly soluble in cold, easily soluble in boiling ether and in boiling absolute alcohol, the solution in the last liquid solidifying to a crystalline mass as it cools. It contains 84·66 p. c. C., and 14·28 H. (Malaguti). To this place probably belongs also Walter's paraffin from ozocerite, which contains 84·62 p. c. C. and 14·28 H., and is not affected by oil of vitriol.

Ozocerite from Obora dissolves in *nitric acid* of sp. gr. 1·34, after boiling for some days, yielding camphretic acid $C^{20}H^{14}O^{14}$ (Schwanert, *Ann. Pharm.* 128, 122). Hofstätter obtained from recrystallised ozocerite from Gallicia, on boiling with nitric acid for several days, the same products as from paraffin, viz., succinic, butyric, and valerianic acid.

According to Hermann, the substance known as *Neftgil* or *Nefte dagil* is identical with ozocerite. It is a body which is brittle at 10° and of the hardness of wax at 15°, obtained by the Tartars of the island of Tschelekän, by burning a thick earth-oil. Its sp. gr. is 0·956; its melting point 81°; at a high temperature it distils almost without alteration. Boiling alcohol dissolves about a third, forming a solution which deposits flocks of wax on cooling. Boiling ether softens it, but dissolves very little. Rock-oil and oil of turpentine dissolve it entirely. By dry distillation it yields oils and a buttery distillate, from which Hermann's *keron*, a substance resembling, but distinct from, paraffin, may be obtained, either by pressing or by agitation with cold ether, in which keron is insoluble, or by boiling with alcohol, from which it crystallises. Keron, after repeated distillation, is white, of sp. gr. 0·893, and melts at 67°; on cooling it solidifies to a crystalline brittle mass. It dissolves in 90·5 parts of boiling alcohol, forming a solution which solidifies on cooling; with difficulty in ether, but easily in fixed and volatile oils. When heated with 3 parts of oil of vitriol, it carbonises and evolves sulphurous acid, but does not distil (Hermann, *J. pr. Chem.* 73, 220; *Chem. Centr.* 1858, 500). *Kir*, from Baku, and *Baikerite* are also similar substances. (See Fritzsche & Hermann, *loc. cit.*).

The meteoric stone of Kaba and that of the Cape contain an easily fusible carbonaceous substance resembling ozocerite (Wöhler, *Ann. Pharm.* 109, 349; 110, 370). The substance sent from Rio de Janeiro to Milan as ozocerite, and examined by Bertolio (*Kopp's Jahresb.* 1860, 797), evidently does not belong to this place.

Chrysogen.

J. Fritzsche. *Petersb. Acad. Bull.* 9, 406; *Krit. Zeitschr.* 9, 139.

A solid hydrocarbon from coal-tar, found in the deposit which separates from the heavy coal oils.

Fritzsche frees the deposit from liquid and easily fusible products by pressing it, while hot, till the residue forms a hard cake, which is made up of white and yellow substances. When this cake is exhausted many times with 90 p. c. alcohol, the latter extracts deposit a yellow pulverulent substance, consisting of microscopic laminæ, which when boiled for a few minutes with 100 times its weight of strong alcohol, and strained after ten minutes, leaves a yellow powder undissolved. When this powder is treated repeatedly with boiling alcohol and afterwards crystallised from benzol and ether, the chrysogen forms the least soluble portion of the crystals.

Chrysogen crystallises from benzol in fine orange-coloured laminæ and irregular tables; from boiling alcohol in small rhombic tables which are rose-red when very thin and appear gold-green by reflected light. It contains 2·32 p. c. of ash, and 94·31 to 94·97 p. c. C., and 5·69 to 4·70 H.

Chrysogen melts at 280° to 290°, but is partially carbonised and volatilised at that temperature. The sublimate is yellowish-green and differs from chrysogen. In a current of air, a sublimate of unchanged chrysogen is obtained. — Its solutions are rapidly bleached by *sunshine.* — It dissolves in *oil of vitriol* with grass-green colour; water throws down from the solution a precipitate from which benzol extracts chrysogen, leaving charcoal. — It is violently attacked by *nitric acid* and converted into an oil which subsequently solidifies.

Chrysogen dissolves very slightly in boiling *alcohol* and *ether;* in 10,000 parts of cold, and 2,000 parts of boiling *glacial acetic acid;* in

2,500 parts of cold and 500 parts of boiling *benzol.*—It colours solid hydrocarbons, to which it is added in small quantity, intensely yellow. It combines with a neutral body obtained by the action of nitric acid on anthracene (xvi, 166) to form olive-coloured needles having a golden lustre.

Oxyazo-nucleus $C^{60}NH^{45}O^{14}$.

Aconitine.

$$C^{60}NH^{47}O^{14} = C^{60}NH^{45}O^{14},H^2.$$

GEIGER & HESSE. *Ann. Pharm.* 7, 276; *Geiger's Handbuch der Pharmacie*, 4 Aufl. 1, 1013.
v. PLANTA. *Ann. Pharm.* 74, 257; *Pharm. Centr.* 1850, 561; *Chem. Gaz.* 1850, 349; *Kopp's Jahresber.* 1850, 434.
HOTTOT & LIÉGEOIS. *N. J. Pharm.* 43, 130; *Pharm. Viertelj.* 13, 273; *Krit. Zeitschr.* 7, 593: *N. Jahrb. Pharm.* 21, 32; *Chem. Centr.* 1864, 558; *Chem. News*, 8, 200; *Kopp's Jahresber.* 1863, 450.
HOTTOT. *N. J. Pharm.* 45, 169 and 304; *Kopp's Jahresber.* 1863, 451.
PROCTER. *N. Jahrb. Pharm.* 23, 27.
C. FRISCH. *N. Jahrb. Pharm.* 23, 140.

Discovered by Geiger & Hesse in 1833, Buchner (*Taschenb.* 1812, 121) having previously endeavoured unsuccessfully to isolate a volatile acid principle from *Aconitum medium*, and Pallas (*J. Chim. méd.* 1, 192) a vegetable base from *Aconitum Lycoctonum*.

Source. Aconitine occurs in *Aconitum Napellus* and probably in all acrid aconites (Geiger), though, according to Geiger, the taste of the herb of *Aconitum Napellus* compared with that of aconitine, shows that this plant contains some other acrid burning substance differing from aconitine. See xiv, 471. Schroff (*Schweiz. Pharm. Wochenschr.* 1865, 205 and 213) likewise distinguishes an acrid and a narcotic principle in aconites. According to him, the former is found exclusively or chiefly in the root of *Aconitum ferox*, and forms the extremely poisonous aconitine of Morson, of which 8 to 10 milligrammes killed a rabbit in six minutes, whilst 400 milligrammes of a German aconitine had been given previously to the same rabbit without endangering its life, and with the production of different morbid symptoms.

Amongst indigenous aconites, *A. Napellus* is said to contain chiefly the acrid, but also some of the narcotic principle; *A. Lycoctonum*, a large quantity of the narcotic principle in the root, but none of either in the herb; *A. variegatum* and *A. paniculatum*, little of either. *A. Anthora* is said to be free from the acrid, and to contain little of the narcotic principle. Now, however, that H. and J. Smith (*Pharm. Jour.* 5, 317; *Pharm. Viertelj.* 13, 548) and Jellett (*Chem. News*, 1864; *Pharm. Viertelj.* 13, 592) have shown that the root of *A. Napellus* contains narcotine (formerly described as *aconelline*), this substance would seem to be the narcotic, and aconitine the acrid principle, of Schroff, whilst Geiger's supposition as to a second acrid principle appears to be erroneous. In any case, however, Geiger and Hesse, as well as v. Planta, examined a peculiar vegetable base free from narcotine, so that

Hottot's statement that aconitine had not been prepared in the pure state previous to his investigation can only apply to some commercial varieties of aconitine. — Neither is Hubschmann's *napelline* (see below) identical with narcotine, inasmuch as no crystals are obtained from its aqueous or alcoholic solutions, or from solutions neutralised with acids (Hubschmann, *Pharm. Viertelj.* 14, 101); but, on the other hand, Morson's *napelline*, which, according to Hottot, is crystallisable and less active physiologically than aconitine, may be identical with Smith's base (Kr.). — Hübschmann obtained from *A. Lycoctonum* two alkaloïds differing from all the above. See pp. 177, 178.

Preparation. 1. Aconitine is obtained from the dry leaves of *Aconitum Napellus* in the same way as atropine is obtained from belladonna (Geiger & Hesse). See xvi, 449. — 2. The root of *A. napellus* is digested for a week with 80 p. c. alcohol containing a little sulphuric acid; the tincture is distilled; the residue is freed from a green oil which floats upon it by decantation and by agitation with ether; the acid solution is mixed with excess of magnesia; and the aconitine thereby set free is taken up by ether, which leaves it in an impure state on evaporation. The product is partially purified by dissolving it in very dilute sulphuric acid, decolorising with animal charcoal, precipitating with ammonia, and boiling, whereby the precipitate is converted into an easily separated coagulum, which is collected, dried, dissolved in ether, and evaporated. On adding ammonia in small quantities to its solution in sulphuric acid, a precipitate of coloured aconitine is thrown down at first, after the removal of which, an additional quantity of ammonia precipitates the pure alkaloïd (Hottot & Liégeois).

Procter adopts a similar process, but exhausts the root with alcohol, and adds the sulphuric acid to the tincture immediately before agitating it with ether. — Hottot, in a later process, exhausts the powdered root with alcohol free from sulphuric acid; distils off the alcohol (partially ?); agitates the residue with hydrate of lime; precipitates the filtrate with dilute sulphuric acid; evaporates; dilutes with water; removes the green oil by filtration; precipitates the aconitine from the filtered liquid at the boiling heat by ammonia; and purifies as above. According to Frisch, water suffices for the exhaustion of the root. He purifies the acid solutions by precipitating with basic acetate of lead; removes excess of lead by hydrosulphuric acid; and leaves the solution in contact with animal charcoal till that substance has taken up the aconitine. After washing the charcoal with water, the aconitine is extracted from it by means of boiling alcohol. The alcoholic liquid, when supersaturated with ammonia, gives up the aconitine to fusel-oil, which in turn gives it up to acidulated water when shaken therewith. From the aqueous solution the aconitine is precipitated by ammonia (C. Frisch). — According to Morson, it is sufficient to exhaust the alcoholic extract of the dry root with dilute sulphuric acid, render the solution slightly alkaline with ammonia, and purify the aconitine thereby precipitated by dissolving it in alcohol and treating the solution with animal charcoal.

v. Planta purifies commercial aconitine, which he found to be impure and to contain ash, by dissolving it in ether, filtering from brown resin, evaporating the solution to a syrup in a vacuum, mixing the residue with a small quantity of absolute alcohol, and dropping the mixture into water, with constant stirring. The flocks thereby precipitated are collected, washed with water, dried in a vacuum, and further purified, if necessary, by a repetition of the process.

The root of *Aconitum Napellus* contains 0·85 p. c. (Frisch), 0·2 p. c.; the American 0·42 p. c. (Procter), 0·06 p. c. of aconitine (Hottot; Smith).

The narcotine of the root of *Aconitum Napellus* is obtained by evaporating the extract (aqueous or alcoholic?) to a soft paste, exhausting this with alcohol, evaporating the tincture, redissolving the residue in alcohol, and adding to the solution a quantity of lime equal to 1½ p.c. of the fresh root employed. The liquid is then filtered, precipitated with sulphuric acid, and again filtered; the alcohol is driven off; the fat which separates is removed; and the solution is mixed with carbonate of soda till nearly neutral, and allowed to stand for some days, till the narcotine is deposited (H. & T. Smith).

Properties. Colourless and inodorous powder, heavier than water, melting at 80° in a current of air, without loss of weight, to a liquid which solidifies in a perfectly transparent glassy mass. Has a strongly alkaline reaction (v. Planta). Geiger & Hesse obtained it from alcohol partly in white granules, but chiefly in the form of a glassy mass, permanent in the air. It has a very bitter, afterwards burning acrid taste, which however, when the substance is pure, is not so persistent and acrid as that of the aconite-plant. It is extremely poisonous: $\frac{1}{50}$th of a grain dissolved in alcohol kills a sparrow in a few minutes, and $\frac{1}{10}$th of a grain, instantaneously. See above. When introduced into the eye, it produces expansion of the pupil for a short time (Geiger & Hesse). It exerts a slight rotatory action on polarised light (Buignet, *N. J. Pharm.* 40, 252). According to Hübschmann (*Arch. Pharm.* 135, 266) Swiss aconitine, prepared by Geiger's process, is a white amorphous, somewhat coarse-grained powder, which does not adhere to paper, and has a strongly bitter but scarcely burning taste. English aconitine on the other hand, is a fine dirty white powder, which adheres very strongly to paper, and has a burning but not bitter taste. Swiss aconitine becomes soft and plastic in boiling water, and hardens to a brittle substance on cooling. English aconitine immersed in boiling water remains pulverulent and does not melt.

Aconitine heated in very small quantity on platinum-foil, and covered with an object-holder, in the manner described under strychnine (xvii, 483) readily yields a sublimate of round granules and fatty drops, which are free from crystals even after moistening with water. On moistening the sublimate with ammonia, and evaporating, delicate crystals make their appearance, generally in the form of needles crossing at right angles. The same crystals, together with octahedrons, are obtained by similar treatment with hydrochloric acid. Sulphuric and nitric acids likewise produce crystals (Helwig, *Anal. Zeitschr.* 3, 52). See also Erhard (*N. Jahrb. Pharm.* 25, 195).

Dried in a vacuum.			V. Planta. *mean.*
60 C	360	67·54	67·97
N	14	2·62	3·42
47 H	47	8·81	8·79
14 O	112	21·03	19·82
$C^{60}NH^{47}O^{14}$	533	100·00	100·00

Decompositions. Aconitine begins to turn brown at 120°, and when more strongly *heated* decomposes and gives off ammoniacal vapours without volatilising. — 2. When heated on platinum foil, it takes fire, and leaves a shining light charcoal, which burns without residue. — 3. *Oil of vitriol* colours it yellowish, then dirty-red (Geiger & Hesse), violet-red (Hottot). Its solution in sulphuric acid is coloured a dirty-green by bichromate of potash, but is not affected by peroxide of lead (Riegel).

Combinations. — *With Water.* Aconitine precipitated by ammonia in the cold, and dried at a moderate temperature, is a hydrate which melts and gives off 20 to 25 per cent. of water at 85° (Hottot & Liégrois). See the contrary above. —Aconitine is nearly insoluble in *water* (v. Planta). It dissolves in 150 parts of cold, and in 50 parts of boiling water, forming a solution which does not become turbid on cooling (Geiger & Hesse).

With Acids. — Aconitine neutralises acids completely, forming uncrystallisable salts (Geiger & Hesse; v. Planta). An aqueous solution of the hydrochlorate gives with ammonia, potash, and carbonate of potash, white precipitates slightly soluble in excess of the precipitants. Carbonate of ammonia, bicarbonate of soda, and phosphate of soda produce no precipitate (v. Planta). Tartaric acid prevents the precipitation of aconitine by bicarbonate of soda (Riegel). Aconitine precipitated by ammonia from cold solutions is hydrated; that precipitated from boiling solutions is anhydrous (Hottot & Liégrois).

Hydrochlorate of aconitine is precipitated kermes-brown by *tincture of iodine* (Geiger & Hesse); also by *biniodide of potassium* (Wagner).

Hydrochlorate of Aconitine. — One hundred parts of aconitine exposed to a current of dry hydrochloric acid gas and afterwards to a current of air at 100°, take up 15·49 parts, or 2 atoms, of the acid (v. Planta).

			v. Planta.
$C^{60}NH^{47}O^{14}$	533	87·95	86·59
2HCl	73	12·05	13·41
$C^{60}NH^{47}O^{14},2HCl$	606	100·00	100·00

Phosphantimonic acid (xiv, 227) produces an abundant white precipitate in solutions of hydrochlorate of aconitine containing $\frac{1}{1000}$th of the salt (Schulze). *Phosphomolybdic acid* precipitates it pale-yellow and flocculent (Sonennschein). The precipitate dissolves in ammonia-water with blue colour, which disappears on boiling (Trapp, *Russ. Pharm. Zeitschr.* 2, 1; *Kopp's Jahresber.* 1863, 702). — Hydrochlorate of aconitine gives with *iodomercurate of potassium* an amorphous white precipitate (Delffs), and with *mercuric chloride* a white curdy precipitate, soluble in hydrochloric acid and in sal-ammoniac (v. Planta).

Chloroaurate of Aconitine. — Dense, amorphous, yellowish-white precipitate, not perceptibly soluble in hydrochloric acid (v. Planta).

			v. Planta. *mean.*
60 C	360	40·44	40 33
N	14	1·58	
50 H	50	5 61	5·59
Au	196 6	22 08	22·06
4 Cl	141·8	15·93	
16 O	128	14·36	
$C^{60}NH^{47}O^{14},HCl,AuCl^{3}$ + 2aq.	890·4	100·00	

The presence of water in the salt is not established.

Bichloride of platinum does not precipitate hydrochlorate of aconitine (Geiger & Hesse; v. Planta). *Sulphocyanide of potassium* throws down a white precipitate; *picric acid* a yellow precipitate, insoluble in ammonia. *Tincture of galls* and *tannic acid* throw down, on addition of a drop of hydrochloric acid, dense flocks, soluble in a large quantity of hydrochloric acid (v. Planta).

Aconitine dissolves very easily in *alcohol*, less freely in *ether* (Geiger & Hesse). It is soluble in 4½ parts of *chloroform* (Schlimpert), and easily soluble in *benzole* (Hottot & Liégeois).

According to Hübschmann (*Arch. Pharm.* 135, 266) Swiss aconitine dissolves in 2 pts. ether, in 2·6 chloroform, and in 4·25 alcohol, these solvents leaving it on evaporation as an amorphous mass having a vitreous lustre. Cold benzol unites it in resinous drops, and slowly dissolves it. On heating it dissolves quickly, and does not separate on cooling.—English aconitine requires for solution more than 100 pts. of boiling ether, which moreover leaves a brown residue undissolved. The solution deposits small white crystals; 1 pt. of it dissolves in 230 pts. chloroform and 20 pts. boiling alcohol, from which solutions it likewise crystallises. Cold benzol colours it dark, and leaves it in the state of powder; on heating the liquid the aconitine dissolves, and separates on cooling, partly in crystals, partly in the form of powder.

Appendix to Aconitine.

1. *Napelline.*—Obtained from crude aconitine. The crude substance is treated with the smallest possible quantity of pure ether to dissolve out the aconitine; the residue is dissolved in absolute alcohol; the filtered solution is precipitated with neutral acetate of lead; excess of lead is thrown down by hydrosulphuric acid; and the filtrate is evaporated to dryness, with addition of carbonate of potash. The residue is exhausted with absolute alcohol, and the alcoholic solution is decolorised with animal charcoal and evaporated to dryness. [What becomes of the acetate of potash? (Kr.)].—White electric powder, having a bitter, afterwards burning taste. Has an alkaline reaction, and evolves nitrogenous vapours when burnt. Neutralises acids completely. Dissolves in water more easily than aconitine, and is consequently not precipitated from dilute solutions by ammonia. It likewise dissolves more easily than aconitine in weak spirit, but less easily in ether (Hübschmann, *Schweiz. Pharm. Wochenschr.* 1857, No. 5; *Pharm. Viertelj.* 7, 134; *N. Repert.* 6, 421; *Kopp's Jahresber.* 1867, 416).

2. *Acolyctine* and *Lycoctonine.* — From the root of *Aconitum Lycoctonum.* The alcoholic tincture of the root is treated with lime and sulphuric acid, as described in vol. xvi. p. 450, 2 (preparation of atropine); the alcohol is evaporated; the resin thrown down is removed; and the residue is decolorised with bone charcoal, mixed with carbonate of soda to alkaline reaction, and evaporated. The dry mass is exhausted with chloroform (or absolute alcohol), which takes up both alkaloïds; the solution is mixed with a little water; the chloroform distilled off; and the remaining syrupy liquid is shaken repeatedly with ether, which takes up the lycoctonine, whilst the acolyctine is obtained from the lower aqueous layer by evaporation.

Acolyctine. — White alkaline powder, bitter but not acrid, burning without residue on platinum foil. Not coloured by oil of vitriol. — Dissolves easily in water and neutralises acids. Precipitable from its aqueous solution or from solutions of its salts by alkaline carbonates. Ammonia converts the solution into a jelly on standing for some days. Neutral acetate of lead throws down from salts of acolyctine, a white precipitate soluble in excess of the precipitant; basic acetate of lead precipitates the aqueous but not the alcoholic solution. Molybdate of ammonia [phosphomolybdic acid? (Kr.)] occasions a white turbidity in sulphate of acolyctine; chloride of gold throws down a pale yellow, tannic acid a white precipitate. — Acolyctine dissolves easily in absolute alcohol and chloroform. It is insoluble in ether, which precipitates it from its solution in alcohol in the form of a paste, or from dilute solutions as a white precipitate, and from chloroform in drops.

Lycoctonine. — Deposited from its ethereal solution, on evaporation, in dull-white nodules, which are washed with ether and water. — Very bitter; alkaline. Melts on platinum-foil and burns. Turns yellow with oil of vitriol. Dissolves slightly in water, and neutralises acids, forming salts which are precipitated by tannic acid. Dissolves easily in alcohol, from which it is not precipitated by water, and sparingly in ether (Hübschmann, *Schweiz. Pharm. Wochenschr.* 1865, 269).

COMPOUNDS CONTAINING 64 ATOMS OF CARBON.

Primary Nucleus $C^{64}H^{68}$; *Oxyazo-nucleus* $C^{64}N^{2}H^{50}O^{16}$.

Veratrine.

$$C^{64}N^{2}H^{52}O^{16} = C^{64}N^{2}H^{50}O^{16}.H^{2}.$$

Meissner. *Schw.* 25, 377; *N. Tr.* 5, 1, 11.

Pelletier & Caventou. *Ann. Chim. Phys.* 14, 69; *Schw.* 31, 178; *Gilb.* 65, 355; *N. Tr.* 5, 2, 93; *J. Pharm.* 6, 353.

Merck. *N. Tr.* 20, 1, 134.

O. Henry. *J. Pharm.* 18, 663.

Couerbe. *Ann. Chim. Phys.* 52, 368; *J. Pharm.* 19, 527; *Ann. Pharm.* 9, 108.

Ed. Simon. *Berl. Jahrb.* 35, 1, 129. — *Repert.* 65, 195. — *Pogg.* 43, 403.

VASMER. *N. Br. Arch.* 2, 74.
G. MERCK. *Ann. Pharm.* 95, 200; *J. pr. Chem.* 66, 343; *Pharm. Viertelj.* 5, 244; *Kopp's Jahresber.* 1855, 568.
A. DELONDRE. *N. J. Pharm.* 27, 147; *Kopp's Jahresber.* 1855, 569.

La Veratrine, to be distinguished from *le Veratrin.* — Discovered by Meissner and by Pelletier & Caventou almost simultaneously in 1819. — Occurs in sabadilla seeds (to the extent of $\frac{1}{3}$rd per cent.) and in white hellebore root (*Handbuch* viii, 86). — Scattergood (*N. J. Pharm.* 46, 128) obtained from *Helleborus viridis*, veratrine and a peculiar resin possessing an action similar to that of veratrine; probably only a modification of veratrine. See p. 127. According to Righini, it exists in *Scilla maritima.* See xvii, 451.

Preparation. From Sabadilla Seeds. 1. Bruised sabadilla seeds are boiled with water containing sulphuric acid; the solution is precipitated with caustic potash or ammonia; the precipitate is dissolved in boiling alcohol; and the solution is decolorised with animal charcoal and evaporated. The crude veratrine thus obtained forms a brittle, fusible, yellow resin, from a solution of which in water acidulated with sulphuric acid, nitric acid added in drops throws down a black glutinous precipitate. The decanted liquid is precipitated with dilute potash-ley; the precipitate is washed and dissolved in boiling alcohol of 40°; and the solution is evaporated. The substance thus obtained is free from ash, but still contains sabadilline and gum-resin, both of which may be removed by boiling with water; also *le veratrin* of Couerbe, which remains undissolved on treating the residue with ether, whilst the true veratrine dissolves and is recovered from the ethereal solution by evaporation (Couerbe).

2. Sabadilla seeds are exhausted in a percolator with water acidulated with hydrochloric acid, and then with pure water, so long as the liquid running through reddens litmus. The extract thus obtained is precipitated with potash-ley; the precipitate is collected, dried, and triturated with the necessary precautions, and afterwards digested for four hours with twice its weight of ether. The ethereal solution is decanted, and the residue again treated with half as much ether as before; the mixed solutions are then evaporated and the veratrine dried over the water-bath (Delondre).

Older processes. 1. Meissner exhausts sabadilla seeds with moderately strong alcohol; evaporates the tincture; exhausts the extract with water; precipitates the veratrine with carbonate of soda; and washes it with water. — 2. Simon frees the seeds from husks, moistens them with alcohol; grinds, and exhausts with alcohol. The extract remaining on evaporating the tincture is boiled with water acidulated with sulphuric acid; and the liquid is set aside to deposit fatty oil, then filtered, mixed with carbonate of soda, and heated to boiling so long as it froths. The veratrine thus obtained melts to a resin, which is washed with cold water, dissolved in 90 p. c. alcohol, decolorised with animal charcoal, and recovered from the solution by distilling off the alcohol and drying the residue (Simon). — 3. Sabadilla seeds are boiled with water and $\frac{1}{16}$th of their weight of oil of vitriol, and again with water and $\frac{1}{32}$nd of oil of vitriol; and, lastly, with water free from acid;

the mixed decoctions are supersaturated with carbonate of soda and evaporated (without filtering) to an extract, which is diluted while still warm with alcohol, and repeatedly exhausted with that liquid. The tincture thus obtained is freed from alcohol by distillation; the residue is dissolved in dilute sulphuric acid; the filtered liquid is precipitated with a large excess of carbonate of soda, and the veratrine thereby thrown down is purified by again dissolving, precipitating as before, and washing the product (Vasmer). In this way 10 pounds of the seeds yield half an ounce of veratrine. The large quantity of acid employed has the effect of making the decoctions less slimy; without acid the whole of the veratrine would not be extracted. The precipitate first produced by carbonate of soda is not collected, because it contains only a part of the veratrine, the rest remaining in solution (Vasmer). See also Righini's process (*J. Pharm.* 23, 520). — 4. Sabadilla seeds are freed from fat by warm ether, and then boiled with alcohol; the alcoholic liquid deposits wax on cooling, after which it is evaporated, and the residue is dissolved in water, which leaves a little fat. The aqueous solution is partially evaporated; the liquid is decanted from the deposit thereby formed, mixed with neutral acetate of lead, and filtered; the filtrate is freed from lead by hydrosulphuric acid, again filtered, and boiled with magnesia: and the washed precipitate is boiled with alcohol, which is then filtered and evaporated. The yellow pulverulent veratrine thus obtained is dissolved in alcohol and precipitated by water (Pelletier & Caventou). According to Delondre, poisonous substances, which excite violent sneezing, are volatilised when sabadilla seeds are boiled with alcohol, or when crude veratrine is dissolved in hot water containing sulphuric acid, so that the greatest caution is necessary in performing these operations.

Properties. White powder, or resinous non-crystalline friable mass. Melts at 115° (Couerbe), at 50°, and solidifies to a translucent yellow mass on cooling (Pelletier & Caventou). When melted at 100° in a vacuum, it swells up very much and forms a spongy mass, which afterwards melts only at a very high temperature (Pelletier & Dumas). It is inodorous, but the smallest quantity of the powder causes violent and dangerous sneezing. Its taste is very acrid and burning, not bitter. In small quantity it produces the most violent vomiting. When given to animals in doses of a few grains, it causes death from inflammation of the intestines (Pelletier & Caventou). Introduced into the eye, it produces a painful burning sensation (Delondre). It turns reddened litmus blue (Pelletier & Caventou). Does not act on polarised light (Buignet, *Compt. rend.* 52, 1085).

When veratrine is very carefully heated on platinum foil in the manner described under strychnine (xvii, 483), it yields a delicate greenish sublimate, and afterwards a denser whitish or yellowish-green deposit. Under a magnifying power of 160 diameters, the former appears crystalline and consists of rectangular prisms, radiated needles, and laminæ, whilst the latter is for the most part amorphous. The crystalline sublimate is not essentially altered by the addition of a drop of water, and is not coloured by chromic acid; aqueous ammonia converts it into oily drops; dilute sulphuric or hydrochloric acid dissolves it and leaves on evaporation crystals of other forms (Helwig, *Anal. Zeitschr.* 3, 50). (See also, Erhard, *N. J. Pharm.* 26, 129.)

	Dried at 160°.		Pelletier & Dumas.	Couerbe.	G. Merck. *mean.*
64 C	384	64·86	65·76	69·66	64·81
2 N	28	4·73	5·04	5·32	5·50
52 H	52	8·78	8·54	7·65	8·71
16 O	128	21·63	20·66	17·37	20·98
$C^{64}N^{2}H^{52}O^{16}$	592	100·00	100·00	100·00	100·00

According to Pelletier & Dumas, $C^{34}NH^{24}O^{6}$; according to Couerbe, $C^{34}NH^{21}O^{6}$. Merck analysed dried veratrine crystals. See below.

Decompositions. 1. Melted veratrine takes fire when strongly *heated*, and leaves a bulky, easily combustible cinder (Merck), emitting at the same time an empyreumatic, not ammoniacal, odour (Meissner). By dry distillation it yields water and a large quantity of empyreumatic oil (Pelletier & Caventou). — 2. Veratrine turns pale greenish-yellow in *bromine-vapour*, reddish-yellow in vapour of *iodine*, and brown-yellow in that of *chloride of iodine* (Donné). A solution of veratrine in 400 parts of water containing sulphuric acid is not coloured or rendered turbid by chlorine (Lepage, *J. Pharm.* 26, 140) Chlorine produces in [strong (Fresenius)] solutions of veratrine, a white precipitate, which is reddened by oil of vitriol after drying (Schlienkamp). More dilute solutions of veratrine are coloured yellowish by chlorine-water and then faint brown by ammonia (Fresenius).

3. Veratrine cakes together like a resin in oil of vitriol, and dissolves easily to a yellow liquid, the colour of which changes to reddish-yellow, blood-red, carmine-red, and after some time to violet (O. Henry; Fresenius). Oil of vitriol colours G. Merck's crystals a transient yellow, passing to fine carmine-red. Veratrine is coloured orange by cold, scarlet by warm, and wine-red by hot oil of vitriol (Guy, *Anal. Zeitschr.* 1, 93). The colour remains unchanged for two or three hours and then disappears (Murray-Thomson, *Schweiz. Pharm. Wochenschr.* 1861, 259). According to Vasmer, the red colour is produced by fuming, not by ordinary oil of vitriol; it is obtained best with acetate of veratrine, and does not appear in presence of nitric acid. The colour is permanent, but disappears on addition of water; when the quantity of veratrine is very small, a large quantity of oil of vitriol is required to produce it. Solutions containing $\frac{1}{500}$th of veratrine are coloured dark-red, solutions containing $\frac{1}{2000}$th wine-red, and solutions containing $\frac{1}{3000}$th amethyst-red, by fuming oil of vitriol (Vasmer). — The solution of veratrine in sulphuric acid is not affected by peroxide of lead, but is coloured green by chromate of potash, with brisk evolution of gas (Riegel)

4. Veratrine is not coloured by *nitric acid* (Merck; Murray-Thomson). It is not reddened by nitric acid, but is converted into a yellow substance, which explodes when heated (Pelletier & Caventou). Veratrine cakes together in resinous lumps in strong nitric acid. and afterwards dissolves with intense reddish-yellow colour (Fresenius). Stannous chloride colours the nitric acid solution yellow (v. Planta).

Oil of vitriol containing nitric acid, prepared according to xvi, 141, colours veratrine yellow and immediately afterwards brick-red; on adding two or three drops of water, the colour becomes blood-red, changing to cherry-red, which is permanent. If oxide of manganese be now added, the solution exhibits after an hour a dirty cherry-red colour, and when subsequently diluted carefully with 4 to 6 volumes of water, and nearly neutralised with ammonia, it becomes light-brown, or when supersaturated with ammonia, throws down a greenish-brown precipitate (J. Erdmann, *Ann. Pharm.* 120, 188).

5. The colourless solution of veratrine in cold strong *hydrochloric*

acid acquires an intense dark-violet colour on warming [dark-red on boiling (Trapp)], deposits small oily drops, and retains its colour for weeks (G. Merck. Trapp, *N. Repert.* 11. 556; *N. J. Pharm.* 44, 456).

Combinations. With Water. Crystallised or Hydrated Veratrine? — When a dilute solution of commercial veratrine in alcohol as free as possible from water is evaporated over a water-bath, part of the alkaloïd separates in the form of a crystalline powder, the remainder forming a brown resin. After the latter has been washed away with cold alcohol, a solution of the crystalline powder in strong alcohol yields rhombic prisms attaining a length of half-an inch. They are colourless and transparent at first, but on exposure to air they effloresce and become opaque and friable; they also turn opaque and lose their form in boiling water, without melting or dissolving (G. Merck).

Veratrine dissolves very slightly in cold water, and in 1000 parts of boiling water, to which it imparts its acrid taste (Pelletier & Caventou).

Tincture of iodine throws down from hydrochlorate of veratrine a kermes-brown precipitate (Merck, v. Planta). *Biniodide of potassium* precipitates veratrine completely (Wagner).

With Acids. Veratrine neutralises acids completely, forming colourless salts, some of which crystallise, whilst others dry up to gummy masses. When an aqueous acid is neutralised with excess of veratrine and then diluted with water, the liquid again becomes acid (from precipitation of veratrine?) (Pelletier & Caventou). The salts of veratrine give with ammonia, and with caustic alkalis and their carbonates, white flocks, which on standing are partly transformed into groups of microscopic crystals. The precipitate is insoluble in excess of the fixed alkalis, but slightly soluble in ammonia, which deposits it on boiling. Alkaline bicarbonates precipitate veratrine from neutral solutions of its salts after some time, and from acid solutions after the free carbonic acid has escaped (Fresenius). The presence of tartaric acid prevents the precipitation of veratrine from dilute solutions by bicarbonate of potash (Oppermann, *Compt. rend.* 21, 810). Magnesia precipitates acetate of veratrine but incompletely, even on boiling, the filtrate giving the veratrine reaction with fuming sulphuric acid (Vasmer).

Carbonate of Veratrine. — A solution of veratrine in carbonic acid water becomes covered in the air with a pellicle composed of small crystalline prisms, which are insoluble in water, but soluble in alcohol and ether. When dried at ordinary temperatures, the salt loses water and carbonic acid, and becomes opaque. — Alkaline carbonates throw down veratrine free from carbonic acid from solutions of its salts (Langlois, *N. Ann. Chim. Phys.* 48, 502; *Ann. Pharm.* 100, 374).

Phosphate of soda throws down from hydrochlorate of veratrine a flocculent precipitate, easily soluble in hydrochloric acid (v. Planta).

Sulphate of Veratrine. — A. *Neutral.* — Obtained from sulphuric acid and excess of veratrine. The neutral solution, evaporated over oil of vitriol, leaves a colourless friable gum (G. Merck). The salt does not act on polarised light (Bouchardat).

	Dried at 100°.	G. Merck. mean.		Pelletier & Caventou.
64 C	384	59·90	59·47	
2 N	28	4·38		
53 H	53	8·26	8·44	
17 O	136	21·22		
SO^3	40	6·24	6·30	6·23
$C^{64}N^2H^{52}O^{16},HO,SO^3$	641	100·00		

B. *Acid.*—Obtained by triturating veratrine with water and sulphuric acid till it becomes thick and frothy, diluting, and heating the mixture to the boiling-point, with addition of a little sulphuric acid. After two or three days the filtrate deposits crystals, which are collected, washed, and dried between blotting-paper.—Long, very delicate, apparently four-sided needles, which, when heated, melt and lose 2 atoms of water of crystallisation, and soon afterwards carbonize, evolving white fumes which contain sulphurous acid (Couerbe).

			Couerbe.
$C^{64}N^2H^{52}O^{16}$	592	85·79	
2 HO	18	2·62	
2 SO^3	80	11·59	12·86
$C^{64}N^2H^{52}O^{16},2(HO,SO^3)$	690	100·00	

Periodate of Veratrine.—Easily obtained from alcoholic veratrine and periodic acid. It is deposited from the solution on evaporation as a buttery mass, which soon hardens to a resin enclosing crystals visible under the microscope. It contains uncombined periodic acid, as is shown by its behaviour with nitrate of silver (Langlois, *N. Ann. Chim. Phys.* 34, 278; *Ann. Pharm.* 83, 174).

A solution of veratrine in aqueous *iodic acid* or in *chloric acid* leaves on evaporation an amorphous gum (Serullas).—*Iodide of potassium* throws down from hydrochlorate of veratrine a yellowish-white pulverulent precipitate, which coheres in curdy lumps (v. Planta).—Veratrine does not combine with perchloric acid (Bödeker).

Hydrochlorate of Veratrine.—Formed by passing hydrochloric acid gas over veratrine, or by dissolving veratrine in dilute hydrochloric acid and evaporating.—Crystals, shorter than those of the sulphate, very soluble in water and alcohol (Couerbe). Transparent gum (Pelletier & Caventou).

			Pelletier & Caventou.
$C^{64}N^2H^{52}O^{16}$	592	94·19	
HCl	36·5	5·81	4·14
$C^{64}N^2H^{52}O^{16},HCl$	628·5	100·00	

Veratrine combines with *nitric acid* not in excess, without decomposition (Pelletier & Caventou).—It does not combine with chromic acid (André).—*Phosphantimonic acid* (xiv, 227) produces in solutions containing $\frac{1}{1000}$th of veratrine, a dirty-white precipitate (Schulze). *Phosphomolybdic acid* (xiii, 164) throws down pale-yellow flocks (Sonnenschein).

Chloro-aurate of Veratrine.—Terchloride of gold throws down from hydrochlorate [and from dilute acetate (Merck)] of veratrine, a sulphur-yellow precipitate [greenish-yellow (Larocque & Thibierge)], not perceptibly soluble in hydrochloric acid (v. Planta). — The salt is obtained by mixing hydrochlorate of veratrine with excess of gold-solution, washing the precipitate with water, drying, and dissolving it in hot alcohol, which deposits yellow silky crystals on cooling. It is purified by recrystallisation from alcohol (G. Merck).

	Dried at 110°.		G. Merck. *mean.*
64 C	384	41·25	41·18
2 N	28	3·01	
53 H	53	5·69	5·94
16 O	128	13·75	
Au	196·4	21·09	21·01
4 Cl	141·6	15·21	
$C^{64}N^{2}N^{52}O^{16},HCl,AuCl^{3}$	931·0	100·00	

Hydroferrocyanate of veratrine behaves like the codeine-salt (xvii, 35) (Dollfus). — Sulphocyanide of potassium does not precipitate acetate of veratrine (Artus, *J. pr. Chem.* 8, 255), or throws down gelatinous flocks from strong solutions only (Fresenius). According to O. Henry (*J. Pharm.* 24, 194) it occasions a precipitate of light flocks in acetate of veratrine, whilst, according to Lepage, it immediately produces a pulverulent precipitate in a solution of veratrine in water acidulated with sulphuric acid.

Veratrine dissolves easily in *vegetable acids.* — *Rhodizonate of veratrine* is hyacinth-red, and easily soluble in water and alcohol. The *croconate* forms a yellow amorphous bitter mass (Heller, *J. pr. Chem.* 12, 229).

Alcoholic veratrine is not precipitated by alcoholic *picric acid* (Kemp). Picric acid throws down a sulphur-yellow precipitate from hydrochlorate of veratrine (v. Planta).

Veratrine is insoluble in aqueous *alkalis* and only very slightly soluble in *caustic ammonia* (Merck).

It dissolves very easily in cold weak *alcohol,* which leaves it on evaporation in the form of a varnish turning white and pulverulent in contact with water (Merck). According to Cap & Garot it dissolves in 1·5 part of alcohol; according to Delondre, in 11 parts of alcohol of 36°. Commercial veratrine dissolves in almost all proportions of absolute alcohol (Fröhner, *Pharm. Zeitschr.* 1854, 11).

Veratrine dissolves rather less freely in *ether* than in alcohol (Pelletier & Caventou). Dissolves in 6 parts of ether (Delondre); commercial veratrine in 10 parts of ether (Fröhner). Insoluble in ether (Meissner; O. Henry), even when boiling (Merck). — Veratrine dissolves in 1·6 part (M. Pettenkofer), in 8·62 parts of *chloroform* (Schlimpert); in 96 parts of *glycerin* (Cap & Garot); in cold *creosote* (Reichenbach); in 56 parts of *olive oil* (Pettenkofer); in 100 parts of *fat oil* (Cap & Garot, *N. J. Pharm.* 26, 81).

Appendix to Veratrine.

1. Sabadilline.

COUERBE. *Ann. Chim. Phys.* 52, 376; *J. Pharm.* 19, 534; *Ann. Pharm.* 9, 114.

According to Couerbe, this body occurs, together with veratrine, in sabadilla seeds, and is obtained in the preparation of veratrine according to page 179. The water in which the crude veratrine is boiled deposits on cooling, first crystals of sabadilline, and afterwards on evaporation reddish acrid oily drops of gum-resin (Couerbe). When the sulphuric acid extracts of sabadilla seeds prepared by Delondre's process are precipitated by potash-ley, and the liquid, filtered from the veratrine thereby thrown down, is evaporated, there remains a residue from which ether takes up a little veratrine, the rest forming with cold water a solution which deposits crystals of sabadilline together with gum-resin (Delondre).

Simon (*Pogg.* 43, 403) regards sabadilline as a compound of resinate of veratrine with resinate of soda, from which veratrine may be obtained by dissolving it in water acidulated with sulphuric acid, and precipitating with excess of ammonia. According to Hübschmann (*Pharm. Viertelj.* 1, 598), however, sabadilline is a peculiar body.

Sabadilline forms white tufts of small needles, apparently six-sided, of very acrid taste (Couerbe). It does not provoke sneezing (Hübschmann). Has a strongly alkaline reaction. Melts to a brown resinous mass at 200°, and does not sublime at higher temperatures. — The *hydrated crystals* lose 9·535 p. c. of water at 180° in a vacuum (4 at. = 8·89 p. c. HO) (Couerbe).

Dried at 180° *in a vacuum.*			Couerbe. *mean.*
40 C	240	64·17	63·15
2 N	28	7·48	7·95
26 H	26	6·95	6·88
10 O	80	21·40	22·02
$C^{40}N^2H^{26}O^{10}$	374	100·00	100·00

Sabadilline turns black at a high temperature, gives off faint clouds, and leaves a large quantity of charcoal. — *Chlorine* deprives it of hydrogen, and forms a brown friable mass. — *Oil of vitriol* turns it brown, and carbonises it. Hot *nitric acid* converts it into an acid resin, without producing oxalic acid.

Sabadilline dissolves in warm water and crystallises from the solution. — It forms with *sulphuric acid* a salt containing 15·9 p. c. of the acid (Couerbe), the solution of which is not precipitated by ammonia (Hübschmann).

Alcohol dissolves several times its weight of sabadilline, but yields no crystals. The solution of anhydrous sabadilline in absolute alcohol is not alkaline, whereas that of the hydrated substance is strongly alkaline. — Sabadilline is quite insoluble in *ether*.

2. Couerbe's *monohydrate* or *resinigomme de sabadilline* is also obtained in the preparation of veratrine, according to page 179. It is a red resin, melting at 165°, having a very acrid taste and strong alkaline reaction. It is easily soluble in water, and neutralises acids to form amorphous salts, from which it is precipitated by alkalis (!). It dissolves abundantly in alcohol, but only very slightly in ether. — Contains 2 atoms of water more than sabadilline (Couerbe).

			Couerbe. *mean.*
40 C	240	61·23	60·59
2 N	28	7·14	7·13
28 H	28	7·14	7·04
12 O	96	24·49	25·24
$C^{40}N^2H^{28}O^{12}$	392	100·00	100·00

3. Crude veratrine which has been boiled with water and thereby freed from sabadilline and the gum-resin, is resolved by digestion with ether into pure veratrine, which dissolves, and an insoluble residue, Couerbe's "*le veratrin.*" The latter is a brown resin, which melts at 185°, and when more strongly heated gives off nitrogenous decomposition-products. It dissolves in acids, without forming crystallisable salts, and is precipitated from the solutions by alkalis. It is soluble in alcohol, but not in water or ether. Contains, on the average, 65·25 p. c. C., 6·28 N., 7·20 H., and 21·27 O., which numbers do not agree very well with Couerbe's formula $C^{28}NH^{18}O^6$ (by calc. 67·7 p. c. C., 5·6 N., 7·2 H., and 19·4 O.) (Couerbe). This body, dissolved in water containing sulphuric acid, yields a crystalline mass, contaminated with an inseparable resin, the solution of which gives a flocculent precipitate with ammonia (Delondre).

4. Sabadillic Acid.

Pelletier & Caventou. *J. Pharm.* 6, 353; *Ann. Chim. Phys.* 14, 69; *Schw.* 31, 172; *Gilb.* 65, 355.

Acide cevadique.—Occurs in sabadilla seeds. The roots of white hellebore and of meadow-saffron also contain this, or a very similar acid.

Preparation. Sabadilla seeds are exhausted with warm ether; the extract is evaporated; the residual fatty mass containing sabadillic acid is saponified with caustic potash; the soap is decomposed with tartaric acid; and the liquid filtered and distilled, the sabadillic acid then volatilising. The distillate is neutralised with baryta-water and evaporated to dryness, and the residue distilled cautiously with phosphoric acid and a little water.

Properties. White pearly needles, melting at 20°, and subliming undecomposed at a somewhat higher temperature. Smells like butyric acid.

Sabadillic acid dissolves in *water.*—With *acids* it forms *salts* having a peculiar odour. The ammonia-salt precipitates ferric salts white. The acid dissolves in *alcohol* and *ether.*

FIRST APPENDIX TO COMPOUNDS CONTAINING 64 ATOMS OF CARBON.

1. Vegetable Bases,

including those whose existence or formula is not established.
With additions.

1. ANCHIETINE.—From the bark of the root of *Anchieta salubris*, a Brazilian crucifer. The bruised fresh bark is allowed to ferment in the air, and afterwards exhausted with dilute hydrochloric acid; the liquid is precipitated with ammonia; and the anchietine thereby thrown down is purified by crystallisation from boiling alcohol, with the help of animal charcoal, and washed with ether.—Straw-yellow needles, of biting, nauseous taste, inodorous, and faintly alkaline.—It melts on platinum-foil, and volatilises almost entirely. Oil of vitriol colours it violet, then black; nitric acid colours it chrome-yellow, without decomposing it.—It dissolves to a slight extent in boiling water. It neutralises acids; the hydrochlorate forms white needles, which are soluble in boiling water only while moist.—Anchietine dissolves in alcohol, but not in ether (Peckolt, *N. Br. Arch.* 97, 271).

2. ANTHEMINE.—*Anthemis arvensis* contains, according to Pattone (*N. J. Pharm.* 35, 198; *Kopp's Jahresber.* 1859, 404) a crystallisable base which is taken up by boiling water from that portion of the extract which is insoluble in alcohol, and is precipitated from the solution by ammonia.

3. APYRINE.—In the nuts of *Cocos nucifera*, and more abundantly in those of *C. lapidea*. Obtained by exhausting the latter with water containing hydrochloric acid, and precipitating with ammonia.—White powder, inodorous, nearly tasteless, neutral. It does not soften or melt when heated, but evolves vapours smelling like burning hemp, and leaves a residue of charcoal. It dissolves in 600 parts of cold water, forming a solution which does not become turbid when heated. It is soluble in dilute acids; the solution in acetic acid becomes turbid on heating; the nitric and tartaric acid solutions are precipitated by alcohol. The acetate and tartrate may be obtained in crystals (Bizio, *J. Chim. méd.* 9, 595; *J. pr. Chem.* 1, 421). Perhaps phosphate of magnesia and ammonia? (Kr.)

4. ATHEROSPERMINE.—From the bark of *Atherosperma moschatum*, a South Australian drug.

An aqueous decoction of the bark, freed from tannic acid by means of neutral acetate of lead, is precipitated by ammonia, which throws down atherospermine, more of which still remains in the bark. The latter is digested with water containing sulphuric acid, and the liquid is strained, nearly neutralised with soda, and precipitated with ammonia. The two ammonia precipitates are digested with alcohol; the solution is evaporated; the residue is dissolved in dilute hydrochloric acid, and again precipitated with ammonia; and the precipitate is dried, triturated, and shaken with bisulphide of carbon, with which it forms a nearly colourless solution. After again evaporating, the residue is dissolved in weak hydrochloric acid and precipitated with ammonia.

Properties. White or greyish-white, light, strongly electric powder, melting at 128°. Inodorous, tastes bitter, and has an alkaline reaction.

	at 100°.		Zeyer.	
30 C	180	70·87	70·02	71 50
N.	14	5 51	5·59	
20 H	20	7 87	6·52	7 78
5 O	40	15·75	17·87	
$C^{30}NH^{20}O^5$	254	100·00	100·00	

Zeyer himself regards the formula as doubtful.

Atherospermine melts on platinum foil, emits an empyreumatic odour, *takes fire*, and burns. — When *heated* in a tube, it evolves an odour of putrid flesh or herrings. — The colourless solution in *oil of vitriol* turns green on addition of chromate of potash. — In contact with *iodic acid* and a little water, it emits a smell of iodine, and colours the liquid brown. — It colours nitric acid brownish-yellow.

It requires more than 6,000 parts of *water* for solution, but dissolves easily in dilute *acids*, forming solutions which dry up to amorphous pellicles. The aqueous solution of the hydrochlorate gives with ammonia, with caustic alkalis and their carbonates, and with lime-water, precipitates insoluble in excess of the precipitants. The solution is precipitated white by *iodide of potassium*, brownish-yellow by *biniodide of potassium*, dirty yellow by *phosphomolybdic acid* (xiii, 164), white by *corrosive sublimate* (the precipitate dissolves in water), ochre-yellow by *terchloride of gold*, yellow by *bichloride of platinum*, yellow by *nitrate of palladium*. *Ferrocyanide* and *sulphocyanide of potassium* likewise produce white, *picric* and *tannic acids* lemon-yellow and yellowish-white precipitates.

Atherospermine dissolves in 32 parts of *alcohol* of 93° Tr. at 16°, and in 2 parts of the boiling liquid. It is soluble also in *bisulphide of carbon*, *chloroform*, *volatile*, and *fixed oils*, and very slightly in *ether* (Zeyer, *Pharm. Viertelj.* 10, 513).

5. **Betaine** $C^{10}H^{11}NO^4$ — (Scheibler, *Zeitschrift f. Chem.* [2], 2, 297; 5, 539). — An alkaloid contained in beet-root. It may be prepared either from the freshly expressed juice, or from the molasses. 1. The expressed juice, strongly acidified with hydrochloric acid, is precipitated with phosphotungstic acid;* the liquid is filtered immediately; and the filtrate set aside for ten days, during which time pointed nodules and prisms gradually crystallise out. These are washed with water and treated with milk of lime; the liquid is filtered; and the filtrate is freed from dissolved lime by carbonic acid, and evaporated. Fine crystals may be obtained by recrystallising from absolute alcohol over oil of vitriol, and removing the insoluble flocks which are formed.

¶ 2. The molasses of beet-root are mixed with about 2 vols. water, and the solution, strongly acidulated with hydrochloric acid, is mixed at first with only a small quantity of the phosphotungstate, whereby a precipitate is formed consisting chiefly of colouring matters and impurities. On removing this, and adding a sufficient quantity of the phosphotungstate to the filtrate, a second purer precipitate is obtained, which is to be treated as above.

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* Prepared by dissolving the so-called bitungstate of soda in ordinary phosphoric acid, and mixing the solution with hydrochloric acid, whereby a precipitate is formed. The solution filtered therefrom contains the phosphotungstate (Scheibler).

Betaine crystallises from strong alcohol in large highly lustrous hydrated crystals, $C^{10}H^{11}NO^4 + 2HO$, which, on exposure to the air, soon deliquesce to a colourless syrup, and when heated to 100°, or left over oil of vitriol, effloresce and give off all their water. It is inodorous, has a sweetish cooling taste, and does not react on vegetable colours. When heated it swells up, first giving off the odour of trimethylamine, then that of burnt sugar, and ultimately leaving a bulky cinder, which burns away very slowly, but completely.

Betaine is not oxidized by chromic acid, or decomposed by heating with hydriodic acid to 200°—210° in sealed tubes. When boiled with solid *potash* and a little water, it is resolved into trimethylamine, which distils over, and several fixed bases. On leaving the liquid to cool after the trimethylamine has all passed off, then diluting with water, supersaturating with hydrochloric acid, evaporating to dryness, and digesting the residue with absolute alcohol, the hydrochlorates of the fixed bases are dissolved, and remain on evaporating the alcohol. On redissolving them in absolute alcohol, which leaves a small quantity of chloride of potassium, and mixing the solution with terchloride of gold, a sparingly soluble *gold-salt*, $C^{10}H^{17}NO^4,HClAuCl^3$, is precipitated, and may be obtained pure and well crystallised by solution in water. The mother-liquor evaporated over sulphuric acid yields another more soluble hydrated salt in large crystals, which effloresce over sulphuric acid.

Betaine is very soluble in *water;* the saturated solution has a sp. gr. of 1·1177, contains 61·8 p. c. of the anhydrous base, and does not act on polarised light.

Hydrochlorate of betaine, $C^{10}H^{11}NO^4,HCl$, and the *sulphate*, form large crystals, permanent in the air; the *nitrate* crystallises in deliquescent needles.

The *chloro-aurate*, $C^{10}H^{11}NO^4,HCl,AuCl^3$, crystallises in beautiful thin needles or small plates, slightly soluble in cold, easily in hot water. With *platinic chloride* the hydrochlorate of betaine forms two salts, which perhaps differ only in their amount of water of crystallisation. It likewise forms well crystallised double salts with the chlorides of zinc, cadmium, and mercury.

Betaine is isomeric, or polymeric, with trimethylated glycollamide, with butalanine, lactamethane, &c., also with oxyneurine. ¶

6. Chaerophylline. — Obtained as sulphate in crystalline laminae, by distilling the crushed fruit of *Chaerophyllum bulbosum* with water and soda-ley, neutralising the distillate with sulphuric acid, evaporating, and exhausting the residue with ether-alcohol, which leaves sulphate of ammonia undissolved. The crystals burn, when heated, with the odour of nitrogenous bodies; they are very easily soluble in water, and when treated with alkalis emit an odour of chaerophyllum. They are precipitated from their solution in white flocks by tannic acid. In 4 grain doses they are poisonous to pigeons (Polstroff, *N. Br. Arch.* 18, 176).

7. Chlorogenine and Porphyrine. — Occur in an Australian bark of unknown origin. See the description (*loc. cit.*). — To be distinguished from Schunck's chlorogenin (xvi, 65).

Preparation. The comminuted bark is exhausted with water, and the extract evaporated to five times the weight of the bark employed; the liquid is mixed, first with sulphuric acid, and then with mercuric chloride, which precipitates the chlorogenine as chloromercurate, and the precipitate is washed with acidulated water so long as the washings are distinctly coloured by strong nitric acid. The salt is then suspended in water and decomposed by hydrosulphuric acid; the filtrate is concentrated and precipitated with baryta-water; the precipitate, which is at first yellow, and changes to brown, is exhausted with absolute alcohol; the tincture is neutralised with dilute sulphuric acid; and after addition of water the alcohol is distilled off. From the remaining sulphate of chlorogenine, ammonia throws down a portion of the chlorogenine as a yellowish-brown precipitate, whilst the greater part remains in solution.

The porphyrine remaining in solution after the precipitation of the chlorogenine by mercuric chloride, is obtained as follows:—The filtrate is freed from mercury by hydrosulphuric acid, neutralised with ammonia, concentrated, mixed with soda-ley, and shaken with ether, which takes up porphyrine and colouring matter. The porphyrine is taken up from the ethereal solution by agitating it with dilute sulphuric acid, then liberated by caustic soda, again taken up by ether, decolorised with animal charcoal, and obtained pure by evaporation.

a. Chlorogenine. — Amorphous coffee-brown powder, very bitter, and apparently poisonous. It turns reddened litmus blue.

	at 100°.		Hesse. *mean.*
42 C	252	65·97	65·77
2 N	28	7·33	
22 H	22	5·75	5·81
10 O	80	20·95	
$C^{42}N^2H^{20}O^8$ + 2aq.	382	100·00	

After deduction of 1·5 p. c. of ash.

Chlorogenine puffs up when *heated*, evolves yellow vapours, and burns with luminous flame. — It yields a volatile base by distillation with *potash-lime*.

It dissolves in *water*, with difficulty in the dry state, but easily when freshly precipitated, and is thrown down from the solution as a yellow precipitate by strong aqueous *ammonia*. It is easily soluble in weak ammonia. — Dissolves (with difficulty when dry) in *acids*, forming neutral amorphous salts. Solutions of the salts containing excess of acid exhibit a blue fluorescence. Ammonia throws down a part of the chlorogenine from its salts, in the form of a yellowish-brown precipitate resembling ferric hydrate. The aqueous salts are not affected by strong hydrochloric acid or by oil of vitriol: nitric acid produces a milky turbidity, and throws down a brown resinous nitrate.

Sulphate of Chlorogenine. — Brown amorphous mass, easily soluble in water and alcohol. Faintly acid.

Hydriodate of Chlorogenine. — Iodide of potassium throws down from acid solutions of chlorogenine a bright yellow precipitate, which changes to a brown resin, soluble with yellow colour in water.

Chromate of Chlorogenine. — Thrown down by bichromate of potassium from the acid sulphate, in the form of a yellow precipitate which turns ochre-coloured on drying. It undergoes alteration on exposure to light and when highly dried. Dissolves with yellow colour in water.

	Dried at 90°,		Hesse.
	or over oil of vitriol.		*mean.*
42 C	252	53·25	53 19
2 N	28	5·91	5·58
21 H	21	4·44	4·56
2 Cr	52·2	11·02	11·02
15 O	120	25·38	25·65
$C^{42}N^{2}H^{20}O^{8},HO,2CrO^{3}$	473·2	100·00	100·00

Chloromercurate of Chlorogenine. — Bright yellow precipitate, soluble in pure but not in acidulated water, and easily soluble in alcohol.

	at 100°.		
$C^{42}H^{21}O^{8}$	337	62·89	
2 N	28	5·22	5·23
2 Cl	71	13·24	13·16
Hg	100	18·65	18·71
$C^{42}N^{2}H^{20}O^{8},HCl,HgCl$	536	100·00	

Chloroplatinate of Chlorogenine. — Brownish-yellow precipitate, fawn-coloured after drying. Contains 17·18 p. c. of platinum, corresponding to the formula $C^{42}N^{2}H^{20}O^{8},HCl + PtCl^{2}$ (by calc. 17·31 p. c. Pt.).

Chloro-aurate of Chlorogenine. — Thrown down from the sulphate by terchloride of gold in the form of a yellow amorphous precipitate.

Chlorogenine dissolves in *alcohol*, and with especial facility in *chloroform*, to a brown-red liquid, which appears deep-green by reflected light. It dissolves in *fusel-oil*, and sparingly in *ether*.

b. Porphyrine. — Crystallises from alcohol in thin white prisms. Tastes very bitter, and has a strongly alkaline reaction. Melts at 82° to a yellowish liquid, which solidifies in an amorphous mass.

Porphyrine evolves alkaline vapours when *heated*, and burns with a bright flame. — It is coloured purple-red by *nitric acid*, even in very dilute solutions. — *Bichromate of potash* colours the acid solution blood-red, and then throws down a yellow precipitate.

It is soluble in cold, and more freely in hot *water*. — With *acids* it forms neutral bitter salts, which in presence of excess of acid, reflect light of blue colour. Ammonia throws down from the salts a white amorphous precipitate.

The *sulphate* dissolves easily in water and alcohol, and appears to crystallise. — *Iodide of potassium* throws down from concentrated solutions of the sulphate, a yellow precipitate; *tannic acid*, a white amorphous precipitate. — *Mercuric chloride* throws down from the hydrochlorate, amorphous white flocks, which crystallise from alcohol in white prisms. — The *chloroplatinate* is a yellowish white, the *chloro-aurate* a yellow precipitate.

Porphyrine dissolves easily in *alcohol* and *ether*, crystallising only from the former liquid (O. Hesse, *Ann. Pharm. Suppl.* 4, 40).

8. Cicutine. — From *Cicuta virosa.* When the fresh roots are triturated with water and expressed, and afterwards exhausted with acidulated water, and the extracts are evaporated and distilled with potash, a distillate is obtained which has the odour of cicuta, and on which there floats a yellow pellicle (Polex, *N. Br. Arch.* 18, 174). — The seeds yield by distillation with potash, an alkaline distillate having a disgusting odour. The expressed juice of the plant, freed from albumin by boiling, yields aqueous cicutine with a little ammonia (Wittstein, *Repert.* 68, 19). — According to Buignet (*N. J. Pharm.* 40, 252) cicutine rotates polarised light to the right; $[\alpha]$ r = 15·9°.

¶ 9. Codamine $C^{38}NH^{23}O^6$ (Hesse, *Ann. Pharm.* 153, 56; *Chem. Centr.* 1870, 167). A base contained in small quantity, together with several others, in the aqueous extract of opium.

Preparation. The aqueous extract is precipitated with excess of lime or carbonate of soda; the liquid separated from the precipitate is agitated with ether, and the ethereal extract is mixed with acetic acid. After removing the ether, the acid solution is poured in a thin stream into moderately dilute potash- or soda-ley, the alkali being kept in excess, and the liquid stirred to prevent the caking together of a resinous precipitate (P) containing papaverine and thebaine. This precipitate is separated after 24 hours, and the filtrate, after supersaturation with hydrochloric acid, is immediately mixed with ammonia, whereby a flocculent precipitate is produced, then with chloroform without previous filtration, and the chloroform solution is treated with acetic acid. After removal of the chloroform, the acid solution is exactly neutralised with ammonia, whereby a reddish, resinous, quickly crystallising precipitate is formed, containing *lanthopine.* After 24 hours the yellowish solution is decanted, filtered, and added to the smallest quantity of potash-ley sufficient to precipitate it (this quantity must, however, be large enough to decompose all the acetate of ammonia in the liquid, and leave an excess sufficient to precipitate the bases). The potash-solution thus obtained is turbid from separated *codeine,* which may be completely removed by agitating the liquid with ether, as it is much more soluble in ether than the other bases; the latter indeed are not taken up by the ether till they have been set free by sal-ammoniac. The ethereal solution left to evaporate very slowly in a tall narrow cylinder, yields in the first place a crystallisation of *laudamine;* and on diluting the mother-liquor with a little ether, washing with aqueous bicarbonate of soda, and leaving the ether to evaporate, crystals of *codamine* are very soon deposited.

Codamine recrystallised from ether forms large colourless six-sided prisms mostly terminated by domes. Melts at 121° and solidifies in the amorphous state on cooling; decomposes at a higher temperature. Tasteless.

	Dried at 100°.		Hesse.
38 C	228	72·84	72·77
N	14	4·47	4·35
23 H	23	7·34	7·29
6 O	48	15·35	15·59
$C^{38}NH^{23}O^6$	313	100·00	100·00

Codamine is easily soluble in boiling water, forming an alkaline solution. It neutralises *acids*, forming amorphous bitter salts. It dissolves in strong *nitric acid* wth dark green, and in strong *sulphuric acid* with blue colour becoming green and afterwards dark violet, when the solution is heated. *Ammonia* and *potash* produce in codamine-salts a white flocculent precipitate soluble in excess.

Chloroplatinate of codamine is a yellow, amorphous precipitate sparingly soluble in water and hydrochloric acid, and yielding by analysis 18·87 p. c. platinum, the formula $C^{38}NH^{23}O^6,HCl,PtCl^2$ requiring 19·02 p. c.

Codamine dissolves easily in *alcohol* and *ether*, still more in *chloroform* and *benzol;* all these solutions have an alkaline reaction. ¶

10. CRYPTOPINE.—An alkaloid of opium, contained in the liquids from which morphine has been precipitated in the preparation of that base. The liquid is freed from alcohol and mixed with milk of lime, and the pasty precipitate thereby produced is exhausted with alcohol, which on cooling deposits the cryptopine in the form of a white crystalline mass. This is dissolved in dilute hydrochloric acid, and the solution set aside to crystallise, whereupon hydrochlorate of thebaine first separates, and after some weeks hydrochlorate of cryptopine crystallises out, and is purified by 6 or 7 times repeated crystallisation.—Small, strongly alkaline crystals, which are coloured by oil of vitriol a fine blue, changing to green on addition of nitrate of potash. The salts are crystallisable, and have a bitter, peppermint-like taste; their solutions readily gelatinize.—The alkaloïd dissolves in 1200 parts of cold, and more easily in hot water; it is insoluble in aqueous alkalis and in ether (T. & H. Smith, *Pharm. Journ.* 6, 240; 8, 595; *Schweiz. Pharm. Wochenschr.* 1867, 136).

11. CYNAPINE.—*Aethusa Cynapium* contains a vegetable base, which crystallises in rhombic prisms, dissolves in water and alcohol, but not in ether, and forms with sulphuric acid a salt crystallising in prisms (Ficinus, *Kastn. Arch.* 11).—On distilling the seeds with lime and water, an alkaline distillate is obtained, which, when evaporated to dryness with sulphuric acid, yields sulphate of ammonia and a salt soluble in ether-alcohol. From the latter salt the base is set free by caustic potash. It smells like conine or nicotine, decomposes metallic salts, and precipitates tincture of iodine (Walz, *N. Jahrb. Pharm.* 11, 351).

12. CYTISINE.—From the ripe seeds of *Cytisus Laburnum.* Chevalier & Lassaigne (*J. Pharm.* 4, 340, and 455; 7, 235) obtained from this source an amorphous bitter substance, which, according to Peschier & Jacquelin (*J. Chim. méd.* 6, 68) occurs also in the leaves of *Coronilla varia.* See also Scott Gray (*N. J. Pharm.* 42, 160).—The unripe seeds of *Cytisus Laburnum* contain laburnine (p. 196).

The aqueous extract, purified by precipitation with basic acetate of lead and highly concentrated, is precipitated with tannic acid; the precipitate is decomposed by drying it with oxide of lead; and the cytisine is extracted from the dry residue by alcohol. For purification it is converted into nitrate, the aqueous solution of which is evaporated to dryness with excess of lead oxide; and the dry residue is exhausted with boiling absolute alcohol, which leaves the cytisine on evaporation.—Colourless crystalline mass, subliming undecomposed between watch-glasses. Has a strongly alkaline reaction.—It deliquesces in the air, neutralises acids, and yields with nitric acid a salt which forms well-defined crystals. The hydrochlorate also forms crystallisable double salts with bichloride of platinum and terchloride of gold (A. Husemann & Marmé, *Krit. Zeitschr.* 8, 161; *Chem. Centr.* 1865, 781).

13. DIOSMINE.—From the leaves of *Diosma crenata.* Deposited from the alcoholic tincture, on standing, in stellar groups of crystals, which taste very bitter and like mint, and emit the odour of the leaves when chewed. Combustible. Insoluble in water; soluble in dilute acids, from which it is not precipitated by alkalis; slightly soluble in weak spirit, freely in ether and volatile oils (Landerer, *Repert.* 84, 62).

14. ERGOTINE.—The active constituent of ergot of rye.—a. *Ergotine of Wiggers.*—Extracted by alcohol, together with mycose (xv, 301), and vegetable osmazome, from ergot of rye previously freed from fat by ether.—Red-brown powder, resembling cinchona-red, and having a peculiar odour becoming more distinct on warming, and a bitter aromatic taste. According to Ludwig, it probably contains nitrogen, and may be regarded as a modified albumin.

When heated it emits a peculiar smell, carbonises, and burns without melting. It dissolves in oil of vitriol, forming a reddish-brown solution, from which it is precipitated in grey flocks by water. The alcoholic solution is bleached by chlorine, with separation of white flocks.—It is insoluble in water, and in aqueous solutions of alkaline carbonates, but dissolves easily in potash-ley, and is precipitated from the solution by dilute sulphuric acid. It dissolves in alcohol with red-brown colour, and in strong acetic acid, from both of which liquids it is thrown down by water (Wiggers, *Ann. Pharm.* 1, 129).—See also Neidhardt (*N. J. Pharm.* 18, 1), who regards ergotine as resin together with colouring matter; Ingenohl (*N. Br. Arch.* 62, 17).

According to Bonjean (*N. J. Pharm.* 1, 174: *Berz. Jahresber.* 27, 481) Wiggers's ergotine is medicinally inactive. Active ergotine is contained in the aqueous extract of ergot, together with albumin which may be removed by boiling, and other substances the separation of which Bonjean does not describe. It forms a reddish-brown extract, having a pungent bitter taste, styptic but not poisonous, soluble in water, insoluble in alcohol and ether.

b. *Ecboline, Ergotine, and Ergotic acid of Wenzell.*—An aqueous infusion of ergot of rye, prepared with cold water, is precipitated with neutral acetate of lead; the filtrate is freed from excess of lead by hydrosulphuric acid; the liquid is concentrated; and powdered mercuric chloride is added thereto, so long as a precipitate is produced. From this precipitate, after washing, decomposing with hydrosulphuric acid, and filtering off the mercuric sulphide, hydrochlorate of ecboline is obtained.—The liquid filtered from the mercuric chloride precipitate gives with phosphomolybdic acid a precipitate containing ergotine, which body is obtained by warming the precipitate with carbonate of baryta, filtering, and evaporating the filtrate.

Both alkaloïds are amorphous, brown, and slightly bitter. They have an alkaline reaction, and burn when heated, emitting an odour of flesh. Ecboline is poisonous; it dissolves in nitric acid without alteration; oil of vitriol colours its solution dark rose-red. — Both form amorphous salts, and are precipitated by phosphomolybdic acid, tannic acid, and terchloride of gold. Bichloride of platinum precipitates ecboline dark-yellow, and ergotine (after addition of ether-alcohol) yellowish. Cyanide of potassium gives a white precipitate with ecboline, but none with ergotine. — Both substances are soluble in water and alcohol; insoluble in ether and chloroform.

Ergotic acid passes over, together with formic acid, on distilling the aqueous infusion of ergot with dilute sulphuric acid (Wenzell, *Pharm. Am. J.*, 36, 193; *Pharm. Viertelj.* 14, 18).

On other constituents of ergot of rye, see Ludwig (*N. Br. Arch.*) 114, 193, where may be found also references to the voluminous literature of the subject, and an epitome of older researches.

15. **Eupatorine.** — From the leaves and flowers of *Eupatorium cannabinum*, from which it is obtained by boiling with water containing sulphuric acid, saturating the filtrate with lime, exposing the precipitate to the air till the lime is converted into carbonate, exhausting with alcohol of 40° B., and distilling off the alcohol; the eupatorine is then left as a white powder. — It tastes bitter and pungent When heated it puffs up and burns. It is insoluble in water, but soluble in absolute alcohol and ether. With sulphuric acid it forms a salt which crystallises in silky needles (Righini, *J. Pharm.* 14, 623; *Mag. Pharm.* 25, 98).

16. **Fagine.** — From beech-nuts. The fagine of Buchner and Herberger (*Br. Arch.* 35, 149; *Repert.* 57, 381) is a yellowish-brown tenacious mass, of repulsive odour, susceptible of distillation with water and alcohol, but not alone. — The body obtained by Zanon (*Repert.* 57, 386), by precipitating an emulsion of the press-cake with hydrate of lime, and exhausting the precipitate with alcohol, is a sticky fatty mass, having an alkaline reaction [possibly oleate of lime? (Kr.)]. The volatile base obtainable from beech-nuts is, according to Brandt & Rakowiecki (*Pharm. Viertelj.* 13, 333) trimethylamine.

17. **Fumarine.** — In *Fumaria officinalis*. This plant contains an alkaloid resembling corydaline, soluble in water and alcohol, insoluble in ether, precipitated by basic acetate of lead (Peschier, *N. Tr.* 17, 2, 80). — Hannon treats the bruised herb with dilute acetic acid, evaporates the extract to a syrup, exhausts with alcohol, decolorises the alcoholic solution with animal charcoal, and evaporates, whereupon the acetate of fumarine crystallises in needles. The crystals, when decomposed by an alkali, give a precipitate of fumarine, which crystallises from boiling alcohol. — Pommier precipitates the acetic extract with ammonia, dissolves the precipitate in hydrochloric acid, decolorises, and allows the solution to crystallise. From the hydrochlorate thus purified the fumarine is separated by ammonia. It forms white bitter alkaline crystals, only slightly soluble in water, and yields with acids frothing crystallisable salts. It is soluble in alcohol (Pommier, *N. Repert.* 2, 469; Hannon, *J. Chim. méd.* [3], 8, 705; *Pharm. Viertelj.* 3, 68; *Kopp's Jahresber.* 1852, 550).

18. **Hederine.** — From the seeds of the ivy. An extract of the seeds, made with acidulated water, is precipitated with milk of lime,

and the precipitate is exhausted with alcohol. Very bitter vegetable base (Vandamme & Chevallier, *J. Chim. méd.* 26, 581; *Berzel. Jahresber.* 21, 325). See also xv, 521.

19. Hyssopine. — A crystalline vegetable base, which, according to Herberger (*Repert.* 33, 1) exists in the herb of *Hyssopus officinalis*, though afterwards Trommsdorff (*N. Tr.* 24, 2, 19) and Herberger himself were unable to obtain it, and the former regarded Herberger's crystals as sulphate of lime.

20. Kawahine, or Methysticine. — Occurs in the roots of *Piper methysticum*, the *Kawa* of the Polynesians, together with a soft resin, O'Rorke's kawin. — Cuzent exhausts the coarsely powdered root with alcohol, filters, distils off the alcohol, and allows the residue to crystallise. The crystals are purified by washing with weak spirit and recrystallising from alcohol, with the help of animal charcoal. Long, silky, white needles, which begin to melt at 120°, and melt completely to a colourless liquid at 130°. Tasteless; neutral. Dissolves very slightly in cold, more freely in hot water; in aqueous acids, without combining therewith; and very easily in alcohol and ether. — Kawahine contains 65·85 p. c. C., 5·64 H., and 28·51 O. (Cuzent, *Compt. rend.* 50, 436; 52, 205; *N. Repert.* 10, 410).

Gobley obtained by a similar process, a quantity of nitrogenous crystals, amounting to 1 p. c. of the roots, melting at 130°, free from smell and taste, and not volatile without decomposition. This body is Gobley's methysticine. It dissolves in oil of vitriol and in hydrochloric acid, producing with the former a fine violet, and with the latter a yellow solution. The crystals colour nitric acid yellow and orange. It is insoluble in water, nearly insoluble in cold alcohol and ether, but easily soluble in boiling alcohol and in warm volatile oils. — It contains 62·03 p. c. C., 1·12 N., 6 12 H., and 30·75 O. — The mother-liquor of methysticine yields a soft greenish-yellow *resin of kawa root* (Gobley, *N. J. Pharm.* 37, 20). See also O'Rorke (*Compt. rend*, 50, 436, and 598); Procter (*Chem. News*, 2, 338); Duboil (*N. J. Pharm.* 41, 215).

21. Laburnine. In the unripe seeds and pods of *Cytisus Laburnum*. See Cytisine (p. 193).

The aqueous extract, purified with basic acetate of lead, is precipitated with phosphomolybdate of soda; the flocculent precipitate is dried, together with chalk; and the residue is exhausted with alcohol. The laburnine thereby taken up is purified by converting it into the platinum double-salt, recrystallising, decomposing the hydrochloric acid solution with hydrosulphuric acid, filtering from sulphide of platinum, evaporating to dryness with excess of carbonate of baryta, and exhausting with boiling alcohol, which deposits laburnine on evaporation. — Large hard crystalline concretions, made up of well-formed, thick, clinorhombic prisms, which give off water of crystallisation at 100°. Neutral to vegetable colours; evolves ammonia when treated with cold potash-ley. Forms long slender needles with bichloride of platinum and terchloride of gold, but appears not to combine with acids (A. Husemann & Marmé, *Krit. Zeitschr.* 8, 162; *Chem. Centr.* 1865, 781).

¶ 22. **Lanthopine** $C^{46}NH^{25}O^{8}$ (Hesse, *Ann. Pharm.* 153, 57; *Chem. Centr.* 1870, 168). Contained in aqueous extract of opium.

Preparation. See Codamine (p 192) — This mode of preparation is founded on the fact that lanthopine does not neutralise acetic acid, whereas the other bases present in the aqueous extract form neutral solutions therewith: hence lanthopine is precipitated when the acetic solution of the whole of these bases is exactly neutralised with ammonia.

Properties. White powder, consisting of microscopic prisms, or fan-shaped groups of prisms, sometimes a centimetre long. Tasteless. Does not alter the colour of litmus.

	at 100°.		Hesse. *mean.*
46 C	276	72·82	72·82
N	14	3·69	3·63
25 H	25	6·59	6·70
8 O	64	16·90	16·85
$C^{46}NH^{25}O^{8}$	379	100·00	100·00

Decompositions. Lanthopine heated to 190° turns brown and gradually decomposes.

Combinations. Lanthopine does not neutralise *acids* completely. It is precipitated from the solutions of its salts by potash-ley and *milk of lime*, and redissolved by an excess of the reagents; also by *sal-ammoniac*, like morphine and pseudomorphine; but it differs from these bases in not forming a blue solution with *ferric chloride. Chloroform* extracts it from the lime solution, but not from the potash solution, till after addition of sal-ammoniac. Strong *nitric acid* gradually dissolves it with orange-red colour; strong *sulphuric acid* with faint violet colour.

Sulphate of lanthopine forms extremely thin needles, very much like narceine.

Hydriodate. White amorphous precipitate, melting and ultimately dissolving in hot water; easily soluble in alcohol.

Hydrochlorate. Extremely thin needles, resembling narceine, appearing like a jelly in mass; easily soluble in boiling water; contains 6·85 to 7·10 Cl., and 20·26 HO.; the formula $C^{46}NH^{25}O^{8},HCl + 12HO$ requires 6·78 Cl. and 20·63 HO.

Iodomercurate. White amorphous precipitate, melting in hot water, and then dissolving; soluble also in alcohol.

Chloroplatinate. Lemon-yellow crystalline powder, insoluble in water, alcohol and hydrochloric acid. Contains 16·25 p. c. Pt. and 3·58 HO.; calc. for $C^{46}NH^{25}O^{8}.HCl, PtCl^{2} + 2HO$ = 16·36 Pt. and 2·98 HO.

Lanthopine is nearly insoluble in *alcohol*, even at the boiling heat, and is completely deposited from the hot solution on cooling. It likewise dissolves with great difficulty in *ether* and in *benzol*, but with moderate facility in *chloroform*, from which it is deposited on evaporation in small white prisms.

23. **Laudanine.** $C^{40}NH^{25}O^{6}$ (Hesse, *Ann. Pharm.* 153, 53; *Chem. Centr.* 1870, 167). Contained in small quantity in the aqueous extract

of opium, and prepared as described under *codamine* (p. 192). Crystallises from hot dilute alcohol in stellate groups of small colourless six-sided prisms, terminated at both ends by domes. Melts at 165°; solidifies in the crystalline state on cooling; not sublimable. Tasteless.

	at 100°.		Hesse.
40 C	240	73 39	73 21
N	14	4 28	4 38
25 N	25	7 64	7 68
6 O	48	14 69	14 73
$C^{40}NH^{25}O^6$	327	100·00	100 00

Homologous with codamine $C^{38}NH^{23}O^6$, codeine $C^{36}NH^{21}O^6$, and morphine $C^{34}NH^{19}O^6$.

The *salts* of laudanine have a bitter taste. From their solutions potash and *ammonia* precipitate the base in white amorphous flocks, which soon become crystalline, and dissolve in excess of the precipitant; *chloroform* extracts it from the ammoniacal but not from the potassic solution. Laudanine dissolves in strong *sulphuric acid* with rose-red colour, in strong *nitric acid* with orange-red colour, and in *ferric chloride* with emerald-green colour.

Sulphate of laudanine forms concentric groups of needles, very soluble in water. The *hydriodate* forms groups of white crystals, strung together like a necklace, easily soluble in boiling water. The *hydrochlorate* crystallises in delicate colourless prisms, easily soluble in water and in alcohol, less soluble in solution of common salt. — The *chloromercurate* is a white precipitate, somewhat soluble in boiling water, and separating therefrom in spherical groups of crystals. — The *chloroplatinate* is a yellow amorphous precipitate, easily soluble in water, especially at the boiling heat. Contains 18·04 p. c. Pt., and 3·57 HO; calc. for $C^{40}NH^{25}O^6,HCl,PtCl^2 + 2HO = 17{\cdot}90$ Pt., and 3·26 HO. — *Sulphocyanide of laudanine* forms white crystalline nodules moderately soluble in boiling water. The *oxalate* crystallises in delicate concentrically-grouped, colourless needles, somewhat sparingly soluble in cold water.

Laudanine in the crystalline state dissolves easily in *benzol*, *chloroform* and boiling *alcohol*; sparingly in cold alcohol, still less in *ether* (1 pt. in 540 at ordinary temperatures); in the amorphous state, that is when recently precipitated, it is much more soluble. ¶

24. Lobeline. Lobelic Acid. — From *Lobelia inflata* (*Handbuch* viii, 65). Reinsch's lobeline is obtained by dissolving the extract of the plant prepared with 75 p. c. alcohol, in stronger alcohol, to separate gum, evaporating the solution, exhausting with water, which leaves resin undissolved, and again evaporating. It forms a yellow hygroscopic mass, having an acid reaction, and bitter, afterwards very acrid taste, easily soluble in water and alcohol, but insoluble in ether. Its aqueous solution is rendered darker by ammonia, but is not altered by acids; it yields a brownish-red precipitate with tincture of iodine, and is precipitated also by mercurous nitrate, nitrate of silver, and tincture of galls, but not by other metallic salts (Reinsch, *Jahrb. pr. Pharm.* 5, 292). See also Pereira (*Chem. Gaz.* 1843, 521).

The lobeline of Colhoun (*J. Pharm.* 20, 545; *Repert.* 50, 220), Bastick, and Procter possesses basic properties. — Bastick prepares it in the same manner as arnicine (xvii, 361). Procter exhausts the seeds with acetic acid and alcohol of 28° B., and evaporates to an extract, which is mixed with magnesia and water, and shaken with ether. The lobeline, which remains in the form of an oil on evaporating the ether, is purified by dissolving it in dilute sulphuric acid, treating the solution with animal charcoal, agitating with magnesia and ether, and again evaporating. — Pale-yellow oil, having a strongly alkaline reaction, an aromatic odour, a pungent taste of tobacco, and acting as a narcotic poison. It volatilises with decomposition when heated, and in the free state is decomposed even at 100°. Alkalis also decompose it. It dissolves in water and neutralises acids, forming crystallisable salts, which are soluble in water and alcohol, and precipitated by tannic acid. It dissolves in alcohol and ether (Bastick, *Pharm. J. Trans.* 10, 217; *N. J. Pharm.* 19, 454; *Pharm. Centr.* 1851, 397; *Kopp's Jahresber.* 1850, 437.—Procter, *Pharm J. Trans.* 10, 456; *Kopp's Jahresber.* 1851, 566).

The statements of F. F. Mayer (*Amer. Journ. Pharm.* 37, 209; *Pharm. Viertelj.* 15, 233) concerning volatile lobeline, appear to refer to this body. The aqueous and acid solutions give a brown-red precipitate with biniodide of potassium. Mercuric chloride produces no precipitate in the aqueous solution, but both aqueous and acid solutions give with iodomercurate of potassium a pale-yellow precipitate, slightly soluble in potash-ley. Nitrate of silver produces in the aqueous solution a white precipitate, soluble in ammonia and nitric acid. Terchloride of gold throws down a pale-yellow precipitate, insoluble in hydrochloric acid; and bichloride of platinum a nearly insoluble precipitate, which floats on water. Tannic acid also precipitates the aqueous and acid solutions.

Procter's *lobelic acid* is obtained by precipitating the decoction of the leaves with sulphate of copper, and decomposing the precipitate with hydrosulphuric acid. It is a crystalline body, which precipitates sulphate of copper pale-green, ferric sulphate olive-brown, neutral acetate of lead and baryta-water yellow.

25. Marsdenine. — In *Cynanchum erectum*. Obtained by digesting the fresh bark of the young plant with ether, and leaving the extract to evaporate spontaneously, whereupon long crystals are slowly formed. It is purified by washing with alcohol and water, and recrystallising from ether, with help of animal charcoal. — Four-sided prisms having a bitter acrid taste. Neutral. In doses of $\frac{1}{4}$th of a grain, it acts as a violent emetic. — When heated on platinum-foil it melts to a brown mass, evolves irritating vapours having an alkaline reaction, carbonises, and burns. — It is insoluble in water, but dissolves easily in dilute acids, forming amorphous salts. The acid solutions are precipitated by alkalis and by tannic acid. — It dissolves with difficulty in cold alcohol of sp. gr. 0·82, easily in ether (Landerer, *Répert.* [3], 8, 77).

¶ 26. Meconidine, $C^{42}NH^{23}O^{8}$ (Hesse, *Ann. Pharm.* 153, 47; *Chem. Centr.* 1870, 167). — Contained in the aqueous extract of opium, and remains in solution after the codamine (p. 192) has crystallised out. When the crystals of the latter no longer appear to increase, the mother-liquor is decanted, the bases contained in it are combined with dilute acetic acid, and the acid solution is saturated with common salt, whereby hydrochlorate of meconidine is thrown down, whilst the salts of a fourth base, x, remain for the most part in solution. The meconidine precipitate, which is of resinous consistence, is redissolved in cold water, with addition of a little acetic acid, and again precipitated with common salt, which operation is once more repeated. Lastly, the salt thus purified is dissolved in a small quantity of cold water, the solution is mixed with excess of bicarbonate of soda, and agitated with ether; the ethereal solution is filtered through animal charcoal; and the ether is left to evaporate, whereupon the meconidine remains as a yellowish varnish, very easily dried at 90°.

Properties. Brownish-yellow, transparent, amorphous mass, which, when touched, splits up into innumerable small laminæ, and may be ground to a yellowish powder. Melts at 58°; not sublimable; burns away completely when heated in the air. Tasteless. Its alcoholic solution blues reddened litmus, and neutralises sulphuric, hydrochloric, and acetic acids.

	Dried at 90°.		Hesse.	
42 C	252	71·39	71 28	71·10
N	14	3 97	4 12	
23 H	23	6·51	6 67	6·59
8 O	64	18 13	17 93	
$C^{42}NH^{23}O^{8}$	353	100 00	100·00	

Meconidine is easily decomposed by strong acids, especially if heated. Its solution in dilute sulphuric acid becomes rose-coloured in a few minutes, purple-red in a few hours; at the boiling heat these changes of colour take place immediately. With acetic acid the change is much slower. Ammonia produces in the purple-red solution a dirty-white, very changeable precipitate. Strong sulphuric acid dissolves meconidine with olive-green colour; strong nitric acid colours it orange-red.

The *salts* of meconidine are very unstable. Their dilute solutions have an intensely bitter taste. From the acetic acid solution the meconidine is precipitated by *potash* or *soda* in white flocks, but is redissolved by excess of the reagent, and may be separated from the alkaline solution, after addition of sal-ammoniac, by ether, chloroform, and other solvents. Acids precipitate it from the alkaline solution, but re-dissolve it when added in excess. *Ammonia* likewise precipitates the base, re-dissolves it when added in very large excess, but gives it up to ether or chloroform when agitated therewith. *Lime* reacts in a similar manner. The reaction with potash distinguishes meconidine from rhœadine (p. 206), the salts of which give with potash a permanent crystalline precipitate.

Chloroplatinate of Meconidine is amorphous, yellow, and soon turns reddish; dried at 100° it yields 17·87 to 17·96 p. c. platinum; calc. for $C^{42}NH^{23}O^{8},HCl + PtC^{2}$ = 17·65 p. c.

The chloro-aurate is a dingy, yellow, amorphous precipitate. — The chloromercurate is amorphous, white, but quickly becomes rose-coloured in contact with hydrochloric acid.

Meconidine dissolves very easily in *alcohol*, *ether*, *benzol*, *chloroform*, and *acetone*. ¶

27. MERCURIALINE.—(Reichardt, *Chem. Centr.* 1863, 65; *J. pr. Chem.* 104, 301; *Jahresb.* 1863, 457; 1868, 754). A volatile alkaloid of *Mercurialis annua* and *M. perennis*. By distilling the plant or seeds with excess of lime, passing the strongly alkaline vapours into dilute sulphuric acid, and evaporating, a saline mass is obtained, from which absolute alcohol takes up sulphate of mercurialine. The alcohol is evaporated; the residue distilled with caustic potash; and the distillate is rectified over fused chloride of calcium in a current of hydrogen, and freed from adhering ammonia under the air-pump.

¶ A better mode of separation is to heat the ammoniacal sulphate of mercurialine with water and excess of potash, soda, or lime, while a stream of carbonic acid is passed through the liquid, and thence into two or three empty bottles, the first of which soon becomes hot and causes all the carbonate of ammonia to volatilise, while the carbonate of mercurialine remains. The carbonate of ammonia may also be driven off by heating over the water-bath, but the evaporation must not be carried on to dryness. The carbonate of mercurialine maybe converted into hydrochlorate or oxalate, and on distilling the dry hydrochlorate with lime, the mercurialine passes over in the gaseous form at 100°, and at 140° it is obtained in oily drops. If ether be used for the separation, or if the distillation be performed in a stream of hydrogen, a large portion of the volatile mercurialine will be lost.

Mercurialine is an oily liquid, colourless when fresh-prepared, but soon becoming brown and resinous. It has a penetrating tear-exciting odour, resembling also that of herb mercury, and a decidedly narcotic action; reacts strongly alkaline, and forms white fumes with hydrochloric acid.

From the analysis of its salts, mercurialine appears to have the same composition as methylamine; the latter, however, is gaseous at ordinary temperatures; the salts of the two bases differ also in some respects. As however the existence of an isomeride of methylamine is not easily conceivable, it is most probable that mercurialine consists of methylamine mixed with a small quantity of an oily odoriferous principle, very difficult to separate.

Carbonate of Mercurialine is formed by neutralising the base with carbonic acid, and remains on evaporation (finally in a vacuum) as a white salt, having an intense odour of mercurialis.

The *sulphate* crystallises in stellate groups of needles, which absorb moisture from the air. It dissolves easily in water, but is insoluble in absolute alcohol; the aqueous solution is neutral. (Sulphate of methylamine crystallises with difficulty, and dissolves easily in alcohol of 95 p. c.). Contains 50·0 p. c. SO^3; calc. for C^2H^6NO,SO^3 = 50·0 p. c. — The *hydrochlorate* crystallises in forms of the regular system, deliquesces easily, dissolves in water and in absolute alcohol; the aqueous solution is neutral, contains 52·1 p. c. chlorine; the formula $C^2H^5N.HCl$ requires 52·6 p. c.

The *nitrate* crystallises like sal-ammoniac in long, colourless, very deliquescent, prismatic forms.

Chloraurate of Mercurialine crystallises easily.

Chloroplatinate of Mercurialine. An aqueous solution of the hydrochlorate, oxalate, or other salt of mercurialine, remains clear when mixed with platinic chloride (distinction from ammonia), but on adding strong alcohol, the platinum salt separates at first in small compressed needles, afterwards in beautiful golden-yellow and very regular six-sided plates; larger crystals are obtained by evaporation of the aqueous solution.

			Reichardt. *mean.*
2 C	12·0	5·1	4·8
N	14·0	5·9	5·8
6 H	6·0	2·5	2·7
3 Cl	106·5	44·9	44·9
Pt	98·7	41·6	41·6
$C^2H^6NCl,PtCl^2$	237·2	100·0	99·8

Easily soluble in water, insoluble in absolute alcohol, and in ether.

Oxalate of Mercurialine, obtained by neutralisation, crystallises in oblique rhombic prisms, frequently also, especially on slow precipitation with alcohol, in small six-sided plates. It is very permanent, greasy to the touch, apt to retain a small quantity of moisture, and absorbs it rapidly, without, however, deliquescing when kept in ordinarily closed vessels. A solution of hydrochlorate of mercurialine in alcohol yields a precipitate of this salt on addition of oxalic acid, sometimes, however, only on further addition of alcohol.

			Reichardt.
8 C	48	31·6	31·4
2 N	28	18·4	18·2
12 H	12	7·9	8·4
8 O	64	42·1	42·0
$C^4(C^2H^6N)^2O^8$	152	100·0	100·0 ¶

Feneulle obtained an acrid extractive of *Mercurialis annua*, precipitable by basic acetate of lead, mercuric chloride, and infusion of galls (*J. Chim. méd.* 3, 116).

¶ 28. Papaverine (Hesse, *Ann. Pharm.* 153, 75; *Chem. Centr.* 1870, 170. — See also xvii, 257). — This base is contained in the precipitate P, obtained as described under Codamine (p. 192), and may be separated therefrom by digestion with excess of oxalic acid, whereby oxalate of papaverine is obtained in the crystalline form. It is better, however, first to dissolve the precipitate in acetic acid, remove thebaine by means of tartaric acid, precipitate the mother-liquor of the tartrate with ammonia, and treat the resinous precipitate with a small quantity of alcohol, whereby it is gradually converted into crystals, while an amorphous base passes into the solution. The crystals are dissolved in excess of oxalic acid, and the oxalate is purified by repeated crystallisation from boiling water, till it dissolves without colour in strong sulphuric acid. The oxalic acid is then removed by chloride of calcium, and the bases are precipitated by ammonia, and obtained pure by recrystallisation from hot alcohol.

Properties. Delicate colourless prisms, tasteless, without action on litmus. Melts at 147°, and at a higher temperature turns reddish, and finally decomposes.

	at 100°.		Hesse. *mean.*
42 C	252	71·79	71·77
N	14	3·99	4·26
21 H	21	5·98	6·02
8 O	64	18·24	17·95
$C^{42}NH^{21}O^{8}$	351	100·00	100·00

Former analyses by Merck and Anderson (xvii, 258), give a smaller proportion of carbon, and lead to the formula $C^{40}NH^{21}O^{8}$.

Papaverine dissolves without colour in strong *sulphuric acid* at ordinary temperatures, but the solution when heated becomes dark violet, like a similar solution of codamine or laudanine (pp. 192, 198). Papaverine which had not been completely purified by oxalic acid, dissolved in strong sulphuric acid with very dark colour. It dissolves in *acetic acid*, but does not neutralise it; dilute sulphuric, hydrochloric, or nitric acid, added to this solution, produces a milky turbidity, and ultimate precipitation of the sulphate, hydrochlorate, or nitrate of papaverine; chloride of sodium and chloride of calcium act in like manner, precipitating hydrochlorate of papaverine; nitrate of soda precipitates the nitrate. With a solution of the acetate of a certain degree of dilution, the hydrochlorate and nitrate are obtained in fine crystals. Potash and soda produce in the acetate solution a resinous precipitate, which soon becomes crystalline, and is insoluble in excess of the reagent.

The following salts of papaverine dissolve in strong sulphuric acid, without blue coloration. The analysis of these salts by Hesse gave results in accordance with his formula of the base.

The *hydrochlorate*, $C^{42}NH^{21}O^{8},HCl$, forms large anhydrous prisms, soluble with acid reaction in 37·3 pts. water, at 13°. Analysis, 9·31 p.c. Cl.; calc., 9·16 p. c. The *nitrate* forms anhydrous prisms.

Chloroplatinate, $C^{42}NH^{21}O^{8}.HCl,PtCl^{2} + 2HO$. Dark-yellow precipitate, composed of beautiful prisms; has a silky lustre after drying in the air. Anal., 17·15 to 17·21 p. c. Pt.; 3·16 to 3·41 HO; calc., 17·15 Pt.; 3·13 HO.

Chloromercurate, $C^{42}NH^{21}O^{8},HCl,HgCl$. Colourless, rhombic anhydrous laminæ, containing 19·42 p. c. Hg., and 13·24 Cl.; calc. 19·14 Hg., and 13·57 Cl.

Iodomercurate. Colourless laminæ crystals, soluble in hot alcohol, and separating in the original form on cooling.

Sulphocyanide. Thin, colourless, anhydrous prisms, very soluble in boiling, very sparingly in cold water.—*Acid oxalate*, $C^{42}NH^{21}O^{8}$, $C^{4}H^{2}O^{8}$. Slightly soluble in cold, easily in boiling alcohol or water (1 pt. in 388 of water at 10°). Contains 79·12 p. c. papaverine, and 20·36 $C^{4}H^{2}O^{8}$; calc., 70·59 papaverine, and 20·41 $C^{4}H^{2}O^{8}$.—*Acid tartrate.* Delicate, colourless prisms, easily soluble in water and in alcohol.—*Acid meconate.* $C^{42}NH^{21}O^{8},C^{14}H^{4}O^{14} + 2HO$. Crystallises in small prisms from an alcoholic solution of equivalent quantities of papaverine and meconic acid. Sparingly soluble in alcohol, and very sparingly in boiling water. Gives off its water of crystallisation (3·89 p. c.) at 100°;

calc. for 2HO = 3·16 p. c. The anhydrous salt contains 60·76 p. c. C., and 4·58 H.; calc. for $C^{42}NH^{21}O^{8},C^{14}H^{4}O^{14}$ = 60 98 C., and 4·53 H.

Papaverine dissolves easily in hot *alcohol*, also in *chloroform* and *acetone;* sparingly in cold alcohol and in *ether* (1 pt. in 258 at 10°); easily in *benzol*, especially when warm. ¶

29. Pseudo-papaverine and Papaverosine. The former, called papaverine by Deschamps, is to be distinguished from the papaverine of opium. — These bases occur in the unripe poppy-heads of *Papaver somniferum.*

a. *Pseudo-papaverine.* — Poppy-heads are twice treated with hot water; the infusions are precipitated with neutral and basic acetate of lead in succession; the filtrate is treated with hydrosulphuric acid; and the precipitate is dried, triturated, and exhausted with boiling alcohol of 95 p. c. After distilling the tincture, the residue is evaporated to a syrup over the water-bath, and again exhausted with boiling alcohol, which deposits white crystals of pseudo-papaverine, together with a black resin, on evaporation. The product dries up on paper to a crystalline pellicle.

Short silky needles, having a bitter taste and an acid reaction. Contains nitrogen. Dissolves in cold, and more freely in boiling water; more easily in water containing acids or ammonia, but does not combine with bases. It is not affected by chromate of potash or ferricyanide of potassium. Biniodide of potassium colours pseudo-papaverine blue, and throws down from the aqueous solution a blue, and from the hydrochloric acid solution a brown precipitate. Iodomercurate of potassium does not precipitate the aqueous solution, but throws down from the solution in hydrochloric acid a precipitate insoluble in water. — Pseudo-papaverine dissolves in alcohol, and crystallises from boiling 70 p. c. alcohol. It is insoluble in ether and chloroform.

b. *Papaverosine.* — Poppy-heads, previously exhausted with hot water and dried, are treated with 56 p. c. alcohol; the alcohol is distilled off; the syrupy residue is exhausted with ether; and after distilling off the ether, the remaining green residue is dissolved in water; the solution acidulated with hydrochloric acid is boiled with magnesia; and the precipitate thereby produced is dried and exhausted with boiling alcohol. The crystals which are deposited on evaporation are purified by dissolving them in acidulated water, precipitating with ammonia, and recrystallising from weak spirit. — Colourless, thick, long needles and octagonal prisms, having a faint taste and slightly alkaline reaction. The substance contains nitrogen.

When treated with *oil of vitriol*, it assumes a violet colour, changing to red on warming, and on the addition of nitric acid a dark orange liquid is formed, which colours a large quantity of water. — It dissolves in strong *nitric acid*, with greenish-yellow colour.

It forms with *hydrochloric acid*, which it does not completely neutralise, a gummy salt, a solution of which turns milky, and deposits crystals on addition of ammonia. — Solutions of papaverosine are precipitated yellow by biniodide of potassium, white by molybdate of ammonia [phosphomolybdic acid? (Kr.)], yellow by chromate of potash, white by iodomercurate of potassium, and whitish by bichloride of platinum.

Papaverosine dissolves in alcohol, benzol, and warm olive oil, and crystallises from the solutions. Its solutions in ether and in chloroform do not crystallise (Deschamps, *Ann. Chim. Phys.* [4] 1, 453; *Kopp's Jahresber.* 1864, 446).

30. Pastinacine.—The fresh seeds of *Pastinaca sativa* yield, when distilled with water and potash, an alkaline distillate and a volatile oil. On removing the latter, neutralising the aqueous liquid with sulphuric acid, evaporating, and treating the residue with ether-alcohol, sulphate of ammonia is left undissolved. The solution, when evaporated and again distilled with potash, yields a distillate containing a little ammonia and an alkaloïd smelling of parsnips (Wittstein, *Repert.* 68, 15).

¶ 31. Physostigmine. *Eserine* (xvii, 594). Hesse prepares this base by mixing the recently prepared extract of Calabar beans with an excess of bicarbonate of soda, agitating with ether, treating the ethereal extract with dilute sulphuric acid, passing the liquid through a wet filter, adding an excess of bicarbonate of soda, and again extracting with ether. On evaporating the ether, pure physostigmine (forming a clear, colourless solution in acetic acid) remains behind as a colourless mass, which dries up over oil of vitriol to a brittle substance, becoming soft at 40°, and liquid at 45°. Strongly alkaline. Tasteless. According to Vintschgau (*Wien. Acad. Ber.* 55 [2], 49) it produces violent tetanic convulsions in many amphibia.

	at 100°.		Hesse.
30 C	180	65·45	65·21
3 N	42	15·27	15·52
21 H	21	7·63	7·59
4 O	32	11·65	11·68
$C^{30}N^3H^{21}O^4$	275	100·00	100·00

By prolonged heating to 100°, more quickly in the moist state, physostigmine is decomposed, with formation of a substance which dissolves with red colour in acids. Physostigmine is moderately soluble in *water*, easily in bisulphide of carbon. With water containing *carbonic acid* it forms a tasteless alkaline solution, which, when heated, becomes turbid, and deposits colourless drops of oil, and after prolonged heating turns red, and then leaves an amorphous, cherry-red mass, partly consisting of unaltered physostigmine.

Physostigmine neutralises *acids* completely; its salts are tasteless. The solution in dilute acids, which is colourless at first, becomes red in a short time, and then, if the decomposition has not proceeded far, may be decolorised by sulphuretted hydrogen, sulphurous acid, hyposulphite of soda, and animal charcoal.—The colourless concentrated solution in *acetic acid* is at first clouded by bicarbonate of soda, the base then separating in colourless oily drops, which, after a few hours, become red by oxidation; if, however, ammonia or an alkaline monocarbonate has been used as the precipitant, the reddening takes place instantaneously. If a solution thus altered be shaken up with ether, and dilute sulphuric acid be then added, the liquid turns blue or red, according to the extent to which the decomposition has advanced. Chloride of lime first colours the solution red, but destroys the colour on further addition. The solution of physostigmine in strong nitric acid is yellow; that in concentrated sulphuric acid is first yellow. then olive-green.

Physostigmine added to neutral *ferric chloride* throws ferric oxide. It forms a kermes-brown precipitate with a solution of *iodine* in iodide of potassium, and is precipitated by *tannic acid*, *mercuric chloride*, and *auric chloride*, but not by platinic chloride. — *Potassio-mercuric iodide* forms with salts of physostigmine a white, easily fusible precipitate of the salt $C^{30}N^{3}H^{21}O^{4},HI,2HgI$, containing 23·16—23·46 p. c. Hg., and 43·63 I (calc. 23·33 Hg, and 44·45 I).

Physostigmine dissolves easily in *alcohol*, *ether*, *chloroform*, and *benzol* (Hesse, *Ann. Pharm.* 141, 82; *J. pr. Chem.* 101, 505). ¶

32. **Pyrarine.** — An alkaloïd from the bark of *Pyrus* or *Cratægus Aria*. A saturated decoction of the bark is evaporated to dryness with calcined magnesia; the residue is boiled with absolute alcohol; the alcoholic liquid is filtered hot, and distilled to dryness; and the residue is exhausted with warm water. There then remains a bitter resin easily soluble in alcohol, whilst the aqueous solution, when evaporated to an extract, yields a straw-yellow mass possessing the properties of a vegetable base. It has an alkaline reaction; neutralises acids; does not form crystals with sulphuric acid; is insoluble in ether. — The alkaloïd is also obtained by exhausting the bark with hot alcohol, evaporating, treating the residue with water containing sulphuric acid, shaking the acid liquid with milk of lime, filtering, and boiling the precipitate with alcohol, which takes up the pyrarine (Zanon, *Repert.* 62, 272). The two processes appear to be contradictory (Kr.).

33. **Pyrethrine.** — From *Radix Pyrethri*. The pyrethrine of Gaultier & Parisol (*J. Pharm.* 1818, 49; 1834, 251) is a mixture of three substances. On exhausting the root with ether, evaporating the liquid, and treating the residue with potash-ley, an oily body is dissolved, whilst a very acrid resin remains behind. The latter is soluble in strong alcohol and is precipitated from the solution by water (Köne, *Ann. Chim. Phys.* 59, 328).

34. **Rhœadine** *and* **Rhœagenine.** — Hesse (*Ann. Pharm. Suppl.* 4, 50; *Ann. Pharm.* 140, 145).

a. Rhœadine. Occurs in all parts of *Papaver Rhœas*, in the ripe capsules of *Papaver somniferum*, and in very small quantity in opium.

Preparation. A warm aqueous infusion of the comminuted plant is evaporated to a thin extract, which is supersaturated with soda and agitated with ether so long as that liquid takes up rhœadine. The ethereal liquid is shaken with an aqueous solution of bitartrate of soda, to which it gives up the rhœadine. This solution, after being freed from ether, yields with ammonia a greyish-white precipitate, which quickly turns crystalline, and is to be washed with cold water, dried, boiled with alcohol to remove colouring matter and thebaine, dissolved in acetic acid, decolorised with animal charcoal, and precipitated with aqueous ammonia, or in order to obtain larger crystals, with alcoholic ammonia.

Properties. Small white prisms, very slightly alkaline in alcoholic solution. Tasteless; not poisonous. Melts at 232°, turning brown and subliming in part. In a stream of carbonic acid long white prisms are easily obtained.

	Crystals.		Hesse. *mean* (3).
42 C	252	65·79	65·77
N	14	3·65	3·62
21 H	21	5·48	5·51
12 O	96	25·08	25·10
$C^{42}NH^{21}O^{12}$	383	100·00	100·00

Rhœadine dissolves in *oil of vitriol* with olive-green, and in strong *nitric acid* with yellow colour. — A solution of rhœadine in excess of moderately dilute *sulphuric* or *hydrochloric acid* assumes, on standing for a short time, a fine purple-red colour, a quantity of red colouring matter amounting to about 5 p. c. of the rhœadine being formed, together with rhœagenine as second product. Tartaric and hot acetic acids act in the same manner. The red colour is destroyed by alkalis and restored by acids.

Rhœadine is nearly insoluble in *water*, aqueous *ammonia*, *carbonate of soda*, and *lime-water*. Its colourless solution in dilute hydrochloric acid not in excess gives with *iodomercurate of potassium*, a pale-yellow precipitate, insoluble in acids, and with *mercuric chloride* a white precipitate, soluble in water.

Chloroplatinate of Rhœadine. — Yellow amorphous precipitate, soluble in water and acids. Loses 2·66 p. c. of water at 110°, and contains 16·26 p. c. of platinum ($C^{42}NH^{21}O^{10},HCl,PtCl^2 + 2HO$ requires 2·96 HO and 16·25 Pt.).

Chloro-aurate of Rhœadine forms yellow flocks, which melt to a red resin when heated. — The *tannate* is a white amorphous precipitate.

Rhœadine is nearly insoluble in *alcohol*, *ether*, *chloroform*, and *benzol*.

b. Rhœagenine. O. Hesse (*Ann. Pharm.* 140, 149). Produced by the action of strong acids on rhœadine. After removing, by means of animal charcoal, the red colouring matter formed at the same time, it is precipitated from the solution by ammonia, and purified by crystallisation from hot alcohol.

Small white prisms having an alkaline reaction. Melts at 223° to a colourless liquid, which turns brown and decomposes, without subliming. Tasteless in itself, but very bitter when combined with acids.

	Prisms.		Hesse.
42 C	252	65·79	65·52
N	14	3·65	3·77
21 H	21	5·48	5·44
12 O	96	25·08	25·27
$C^{42}NH^{21}O^{12}$	383	100·00	100·00

Isomeric with rhœadine.

Rhœagenine is slightly soluble in *water* and aqueous *ammonia*. — It dissolves easily, without colour, in acids, which it neutralises completely, forming *salts*. The solution in strong nitric acid alone is coloured yellow.

The *sulphate* is a colourless amorphous salt, having a neutral reaction, easily soluble in water, less freely in alcohol. It gives with *bichromate of potash* a yellow precipitate; with *iodomercurate of potassium* a pale-yellow precipitate, insoluble in acids; and with *mercuric chloride* a white amorphous precipitate, easily soluble in water and acids. — *Chloro-aurate of rhœagenine* is a yellow amorphous powder, insoluble in dilute acids. The *chloro-platinate* is a yellow amorphous precipitate, abundantly soluble in water and in hydrochloric acid: it contains, at 110°, 16·44 p. c. of platinum (by calc. 16·73 p. c. pt.).
Rhœagenine is but little soluble in *alcohol* and *ether*.

35. SARRACININE. — Occurs in the root of *Sarracinia purpurea*. The powdered root is agitated with water acidulated with sulphuric acid; the liquid is evaporated to dryness, and the residue treated with bisulphide of carbon, which takes up a resinous body. The exhausted substance is then treated with water, and the aqueous liquid is evaporated to a syrup and shaken with ether, to which it gives up sulphate of sarracinine. The salt is purified by crystallisation and decomposed with bicarbonate of soda. — Sarracinine is a white bitter substance, forming salts; the sulphate crystallises in needles. It dissolves in alcohol and ether (St. Martin, *Pharm. Viertelj.* 15, 234; and, with some varying statements, *Krit. Zeitschr.* 9, 112).

36. TAXINE. — Obtained from the leaves of *Taxus baccata*. An alcoholic tincture of the leaves is evaporated to dryness, together with tartaric acid. The residue is exhausted with water; and the aqueous solution thus obtained is filtered, evaporated to a syrup, mixed with excess of bicarbonate of soda, and shaken repeatedly with ether, which takes up the taxine and leaves it behind on evaporation. The product is purified by repeatedly dissolving it in dilute acids and precipitating with ammonia. — Loose, non-crystalline, bitter powder, melting to a friable yellow resin when heated. — It dissolves in oil of vitriol with purple-red, and in strong nitric acid with yellowish-brown colour. — It is sparingly soluble in water but easily soluble in dilute acids, with which it does not form crystallisable salts, and is precipitated from the solutions by the fixed alkalis and ammonia. The solution in sulphuric acid is precipitated yellowish-brown by tincture of iodine, white by tannic acid, and is not affected by bichloride of platinum. — Taxine dissolves easily in alcohol and ether (Lucas, *N. Br. Arch.* 85, 145).

¶ 37. THEBAINE. — (Hesse, *Ann. Pharm.* 153, 69; *Chem. Centr.* 1870, 167.) — This base, discovered by Thiboumery (xvii, 167), is one of the constituents of the precipitate P, obtained in treating the aqueous extract of opium in the manner described under *codamine*, (p. 192). By dissolving this precipitate in acetic acid, treating it with animal charcoal, combining it with tartaric acid, recrystallising the tartrate from a small quantity of boiling water, and separating with ammonia, the thebaine is obtained perfectly pure. In this state it crystallises from hot dilute alcohol in beautiful colourless crystalline laminæ; from strong alcohol, in solid prisms. Melts at 193°; not sublimable; tasteless; its solutions have an alkaline reaction.

	Dried at 100°.		Hesse.
38 C	228	73·31	73·22
N	14	4·50	
21 H	21	6·75	6·77
6 O	48	15·44	
$C^{38}NH^{21}O^6$	311	100·00	

This analysis agrees very nearly with that given by Kane (xvii, 168).

Thebaine is nearly insoluble in cold *water*. Its solutions turn litmus blue, and neutralise sulphuric acid; strong nitric and sulphuric acids decompose it immediately, the latter with red colour. — With dilute *sulphuric acid* it yields thebaine and sulphate of thebaicine (see below). From the solutions of its salts it is precipitated by *potash*, *ammonia*, or *lime*, in white amorphous flocks, which soon become crystalline, and dissolve slightly in excess of ammonia or milk of lime. *Bicarbonate of soda* forms a white precipitate consisting of small prisms.

Hyposulphite of Thebaine, produced by decomposing the tartrate with hyposulphite of soda, forms small white prisms, very soluble in cold water, still more in hot water, and in alcohol. — The *hydriodate* obtained by decomposing the neutral tartrate with iodide of potassium crystallises in very delicate colourless prisms, easily soluble in water.
The *hydrochlorate*, $C^{38}NH^{21}O^6,HCl + 2HO$, forms large rhombic prisms having a neutral reaction, soluble in 15·8 pts. water at 10°; the solution gradually turns yellow, especially on boiling; contains 84·67 p. c. thebaine, 9·46 Cl, and 4·73 HO; calc. 85·08 thebaine, 9·71 Cl, and 4·73 HO. — The *chloroplatinate* is a yellow amorphous precipitate, quickly converted into a mass of orange-coloured prisms. Contains 17·50 to 17·99 p. c. Pt., and 6·93 to 7·15 HO; calc. for $C^{38}NH^{21}O^8,HCl,PtCl^2 + 4HO = 17·84$ p. c. Pt. and 6·51 HO. Gives off its water over sulphuric acid, and very easily at 100° (according to Anderson, only 2HO). — The *chromate* forms small yellow prisms.

Oxalates of Thebaine. The *neutral oxalate* $2C^{38}NH^{21}O^6,C^4H^2O^8 + 12HO$, obtained by treating an alkaline solution of the base with oxalic acid, forms cauliflower-like groups of small white prisms, soluble in 9·7 pts. water, at 10°, very soluble in alcohol, insoluble in ether. Gives by analysis 8·68 to 8·81 p. c. C^2O^3, and 13·65 to 13·83 HO; calc. 8·75 C^2O^3, and 13·14 HO. — The *acid oxalate*, obtained by adding 1 equiv. of oxalic acid to the concentrated aqueous solution of the neutral salt, forms large colourless prisms, which give off 44·5 p. c. water at 20°.

Tartrates. — The *acid tartrate*, $C^{38}NH^{21}O^6,C^8H^6O^{12} + 2HO$, forms slender white prisms, easily soluble in hot alcohol and boiling water, sparingly in cold water (1 pt. in 130 at 20°). The solution has an acid reaction and bitter taste. Contains 61·81 p. c. thebaine, and 3·65 to 3·75 HO; calc. 64·92 thebaine and 3·75 HO. — The *neutral tartrate* is obtained by saturating the acid salt with thebaine, removing the uncombined thebaine with ether, and evaporating at a gentle heat, as an amorphous residue, soluble with neutral reaction in water and in alcohol.

Meconate, $2C^{38}NH^{21}O^6.C^{14}H^4O^{14} + 12HO$. — Obtained by dissolving 2 at. thebaine and 1 at. meconic acid in hot alcohol, and evaporating. Stellate groups of colourless prisms, easily soluble in hot alcohol, sparingly in cold alcohol, moderately soluble in boiling water, sparingly in cold water (1 pt. in 304 at 20°). The solutions are neutral. Contains 57·85 p. c. C. and 6·19 H.; calc. 58·06 C. and 6·23 H. Gives off 11·70 to 12·00 p. c. water; calc. 11·61 p. c.

Thebaine dissolves easily in *alcohol*, *chloroform*, and *benzol*, sparingly in *ether* (1 pt. in 140 at 10°).

38. THEBENINE and THEBAICINE. — Bases isomeric with thebaine, produced by the action of acids on the latter.

a. Thebenine is prepared by heating 10 grammes of thebaine with 200 grammes of hydrochloric acid (sp. gr. 1·04) to the boiling point, removing the flask from the fire as soon as the first bubbles of vapour appear, and cooling the solution by pouring it into an equal volume of cold water. Crystals of hydrochlorate of thebenine are thereby obtained, which may be purified by recrystallisation; and from the aqueous solution of this salt the base may be separated as a white flocculent precipitate by addition of sulphite of soda. It is perfectly amorphous, insoluble in *ether* and *benzol*, slightly soluble in boiling *alcohol*, insoluble in *ammonia*, easily soluble in caustic *potash*, and separable therefrom by sal-ammoniac; neutralises *hydrochloric* and *sulphuric* acids. It rapidly absorbs *oxygen*, especially in contact with basic substances. Its solution in *potash* becomes dark brown, from formation of a humus-like, apparently basic substance. Strong sulphuric acid dissolves thebenine with splendid blue colour, which disappears on addition of water, and is reproduced by further addition of the acid.

Salts of Thebenine. — The *sulphate* is obtained pure by heating the aqueous solution of the hydrochlorate with a little sulphuric acid, as a white crystalline powder made up of small prisms. In the air-dried state it contains 2 at. water, which it gives off at 100°.

	at 100°.		Hesse.	*Air-dried.*			Hesse. *mean.*
38 C	228	63·33	63·45	$C^{38}NH^{21}O^6$	311	82·28	
N	14	3·88	3·86	HSO^4	49	12·96	13·09
22 H	22	6·11	6·11	2HO	18	4·76	4·55
S	16	4·44	4·58				
10 O	80	22·24	22·00				
$C^{38}NH^{21}O^6,HSO^4$	360	100·00	100·00	+ 2HO	378	100·00	

Hydrochlorate. — Large colourless crystalline laminæ, very soluble in boiling water and alcohol, sparingly in cold water (1 pt. in 100); dissolves in nitric acid with orange-red colour and evolution of nitrous acid. Has a bitter taste, and does not appear to be poisonous, whereas hydrochlorate of thebaine is a very powerful poison.

	Air-dried.		Hesse.
38 C	228·0	56·79	56·14
N	14·0	3·49	
28 H	28·0	6·97	6·95
Cl	35·5	8·84	8·62
12 O	96·0	23·91	
$C^{38}NH^{21}O^6,HCl + 6HO$	401·5	100·00	

When heated it gives off 13·61 p. c. water; calc. for 6HO = 13·47.

The *chloromercurate*, $C^{38}NH^{21}O^{6},HCl,HgCl + 2HO$, forms very long, colourless prisms, mostly in fan-like groups; contains 14·36 p.c. Cl, 20·12 Hg, and 3·25—3·63 HO; calc. 14·17 Cl, 19·96 Hg, and 3·59 HO. Gives off its water completely over oil of vitriol, very quickly at 100°. The *chloroplatinate* is a brownish-yellow amorphous precipitate, quickly becoming darker, and ultimately converted into a greenish brown mass.

Sulphocyanide of Thebenine separates on adding sulphocyanide of potassium to the aqueous solution of the hydrochlorate, as a white shining crystalline powder, very sparingly soluble in cold water.

Oxalate of Thebenine is obtained by precipitating the hydrochlorate with oxalic acid, in large colourless crystalline laminæ, having a satiny lustre; slightly soluble in boiling water, insoluble in alcohol.

	at 100°.				*Air-dried.*			Hesse.
42 C	252	62·85	62·70	$C^{38}NH^{21}O^{6}$	311	74·23		
N	14	3·49		$C^{4}H^{2}O^{8}$	90	21·48		21·47
23 H	23	5·73	5·50	2HO	18	4·29		4·43
14 O	112	27·93						
$C^{38}NH^{21}O^{6},C^{4}H^{2}O^{8}$	401	100·00		+ 2HO	419	100·00		

6. *Thebaicine* is produced from thebaine, or from thebenine, by the action of strong acids; with hydrochloric acid at the boiling heat the change is complete in a few minutes. The resulting solution, mixed with ammonia, yields thebaicine in the form of a yellow amorphous precipitate. Thebaicine is insoluble in *water*, *ammonia*, *benzol*, and *ether*; slightly soluble in hot *alcohol*, and separates from the solution still in the amorphous state. It dissolves easily in *potash*, and the solution quickly absorbs oxygen from the air; thebaicine alone is likewise sensitive to oxygen. It dissolves in strong *nitric acid* with dark red, and in strong *sulphuric acid* with dark blue colour. The *sulphate* and *hydrochlorate of thebaicine* are amorphous and resinous; the *chloromercurate* is a white amorphous flocculent precipitate. Neither the base nor its salts have been analysed, but from its close analogy to thebaine and thebenine, Hesse regards it as isomeric therewith. ¶

39. TRIANOSPERMINE, *and other constituents of the root of Trianosperma ficifolia, one of the Brazilian Cucurbitaceans.*—An alcoholic extract of the root is exhausted with water, which leaves resins undissolved; the solution is freed from substances precipitable by neutral acetate and basic acetate of lead in succession, and also from excess of lead; and the filtrate is evaporated and freed from the potash salts which crystallise out. To the mother-liquor absolute alcohol is added to precipitate gum; the filtrate is mixed with ether, which throws down sugar; and the liquid is evaporated to dryness. The amorphous residue is dissolved in water; the solution is precipitated with tannic acid; the precipitate is triturated with calcined magnesia, dried, and exhausted with alcohol; and the tincture is evaporated to a syrup and shaken with ether. The ether takes up trianospermitine, which crystallises on evaporation, whilst the syrupy liquid contains trianospermine and bitter substance, the former of which crystallises out on addition of alcohol, and standing, the latter remaining in the mother-liquor.

a. Bitter substance or Tayuyin.—Amorphous, yellow, very hygroscopic mass, having a very bitter taste and a slightly acid reaction, and acting as a purgative. It is combustible. Alkalis convert it into a dark substance, which is precipitated by acids. It dissolves easily in water; baryta-water precipitates the solution yellow; lead salts give a white precipitate only after addition of ammonia. It is precipitated by nitrate of silver, by terchloride of gold, by bichloride of platinum, after addition of alcohol, and by tannic acid, but not by tartar-emetic. It dissolves in alcohol, and to a slight extent in ether.

b. Trianospermine.—Colourless needles, without smell, of a somewhat biting taste and alkaline reaction. Volatilises completely when heated. It dissolves in water, from which it is precipitated by basic acetate of lead and bichloride of platinum, and is soluble also in alcohol and ether.

c. Trianospermitine.—Small white granules, without smell or taste, volatilising when heated. It is insoluble in water, slightly soluble in absolute alcohol, and easily soluble in ether. The (alcoholic ?) solution is precipitated by mercuric chloride and basic acetate of lead.

The root contains also alpha- and beta-resins (Peckolt, *N. Br. Arch.* 113, 104).

40. *Alkaloïd from the seeds of Vitex Agnus castus.*—The alcoholic tincture of the seeds yields a very bitter crystalline mass, nearly insoluble in water, but easily soluble in dilute acetic acid. It is precipitated from its solution in acetic acid by potash and ammonia, and from its alcoholic solution by tincture of galls.—When an extract of the seeds, made with hydrochloric acid, is precipitated with ammonia or magnesia, the precipitate exhausted with alcohol, and the tincture decolorised with charcoal and evaporated, indistinctly crystalline warts make their appearance, which are soluble in acids, are precipitated therefrom by ammonia, and dissolve in ether and alcohol (Landerer, *Repert.* 54, 90).

SECOND APPENDIX TO COMPOUNDS CONTAINING 64 ATOMS OF CARBON.

Bitter Principles and other peculiar Vegetable Substances

chiefly those whose existence or formula is not well established.

With Additions.

1. ACHILLEIN.—Occurs in *Achillea Millefolium.*—The aqueous decoction of this plant is clarified with albumin and concentrated; the liquid is then neutralised with milk of lime, decolorised with animal charcoal, and evaporated; the residue is treated repeatedly with absolute alcohol; and the achillein which remains on evaporating the alcoholic solution is freed from resin by dissolving it in water.—Hard, reddish-brown, hygroscopic extract, neutral, and bitter. It dissolves easily in water, forming a solution which is precipitated by basic acetate, but not by neutral acetate of lead. It is soluble also in boiling strong alcohol, but not in ether; the alcoholic solution is not precipitated by tannic acid (Zanon, *Ann. Pharm.* 58, 21).—The *achilleic acid,*

likewise found by Zanon in yarrow, is, according to Hlasiwetz (*Wien. Acad. Ber.* 24, 268), aconitic acid (xi, 401).

¶ 2. ACORIN. A nitrogenous glucoside contained in the roots of *Acorus Calamus.* The unpeeled roots are repeatedly boiled with water; the extract evaporated down to the weight of the roots is mixed with an equal volume of alcohol; the filtrate is precipitated with neutral and basic acetate of lead; and the liquid, filtered from the precipitate, freed from excess of lead by sulphuretted hydrogen, and from alcohol by distillation, and concentrated to a small bulk, is mixed with excess of soda-ley, and then shaken up with ether. On evaporating the ether, the acorin (still impure) remains as a non-crystalline, honey-yellow, soft, resinous mass, having the bitter aromatic taste of the root. It dissolves easily in ether and in alcohol, and is precipitated from the former by benzol, from the latter by water. It has a slight alkaline reaction in alcoholic solution; dissolves slowly but completely in hydrochloric acid, and is precipitated therefrom by tannic acid, potassio-mercuric iodide, iodine-water, and phosphomolybdate of soda. It reduces auric and platinic chloride, also an alkaline cupric solution, after some time. Boiled with dilute sulphuric acid, or with baryta-water, it yields a resinous nitrogenous substance, together with sugar (Faust. *Arch. Pharm.* [2], 131, 214; *Bull, Soc. Chim.* [2], 9, 392; *Jahresber.* 1867, 753).¶

3. ADANSONIN.—From the bark of *Adansonia digitata* (*Handbuch*, viii, 29). Extracted from the bark by ether, from which it crystallises on evaporation (Walz). Wittstein boils the alcoholic extract of the bark with water, shakes the decoction with oxide of lead, evaporates the filtrate, and treats the residue with ether, which takes up the adansonin.—White needles and prisms, melting to a resin below 100°. Non-nitrogenous. Contains 48·30 p. c. C., 5·95 H., and 45·75 O., and is probably represented by the formula $C^{48}H^{36}O^{33}$ (Walz).—It dissolves in oil of vitriol with brown colour, and turns brown in hydrochloric acid. Nitric acid forms on evaporation a yellow tasteless resin.—According to Walz, it is insoluble, but according to Wittstein, slightly soluble in water. It dissolves in ammonia, forming a yellow solution, from which it is precipitated by acids, and is easily soluble in aqueous and absolute alcohol, and in ether (Walz, *Jahrb. pr. Pharm.* 24, 100, and 242; 27, 1.—*N. Jahrb. Pharm.* 1, 163. Wittstein, *Pharm. Viertelj.* 4, 41).

The red *colouring matter of Adansonia* is extracted by alcohol from the powdered root which has been previously exhausted with ether, and is purified by treatment with water. It forms an amorphous dark blood-red mass, containing 59·21 p. c. C., 6·08 H., and 34·71 O., and dissolves in oil of vitriol with brown-black colour. It is deposited from its solution in boiling water (200 parts) in the form of a red powder, and from its solution in ammonia, on addition of hydrochloric acid, in yellowish-red flocks. Alcoholic neutral acetate of lead throws down from an alcoholic solution of the colouring matter, violet flocks containing 36·30 p. c. PbO., 38·36 C., 3·84 H., and 21·18 O. The alcoholic solution of the colour precipitates metallic salts. The colouring matter is very easily soluble in absolute alcohol, but not in ether (Walz, *Jahrb. pr. Pharm.* 27, 6).

4. AGARICIN.—Occurs in the officinal *Agaricus albus*, the inner

substance of the larch agaric (*Polyporus officinalis*). It is to be distinguished from amanitin (see below) and from the solid fat of mushrooms, which has also been called agaricin (see *Cholesterin*).

When *Agaricus albus* is exhausted by percolation with cold water and 86 p. c. alcohol in succession, the alcoholic extract leaves, on evaporation in a vacuum, an amorphous yellow residue, amounting to 65 p. c. of the agaric employed, and soluble to the extent of $\frac{1}{3}$rd in 50 p. c. alcohol. This solution is allowed to evaporate spontaneously; the white powder which is then deposited is dissolved in strong alcohol; and the solution is mixed with $\frac{1}{4}$th its volume of ether, which precipitates extractive matters. The ether-alcohol solution leaves agaricin on evaporation.—White crystalline powder, made up of microscopic flat prisms. Tastes at first insipid, afterwards sweetish bitter and pungent. Free from nitrogen.—It does not reduce alkaline solutions of copper, either alone or when mixed with emulsin, and left for 12 hours at 40°; but it exerts a slight reducing action after being boiled with dilute sulphuric acid, or after an hour's contact with saliva, a peculiar sugar being apparently produced.—It is dissolved and decomposed by strong acids and alkalis; soluble to a slight extent in water and in alcohol, but not in ether (Schoonbroodt, *Pharm. Viertelj.* 13, 227).

5. Amanitin.—The poisonous principle of *Agaricus bulbosus*, *A. muscarius*, and *A. volvaceus*. The expressed juice is freed from albumin by heating it in a water-bath, then filtered, and precipitated with basic acetate of lead; the filtrate is freed from lead by means of sulphuric acid and evaporated to dryness; the residue is exhausted with ether to remove fat; and the amanitin is taken up by absolute alcohol.—Brown amorphous deliquescent mass, poisonous, inodorous, and tasteless. It is not decomposed by acids or dilute aqueous alkalis, or precipitated by basic acetate of lead or tincture of galls. It dissolves in water, but not in volatile oils or ether (Letellier, *J. Pharm.* 16, 109; *Ann. Pharm.* 25, 196). According to Sicard and Schoras (*N. J. Pharm.* [4] 1, 442) the fungi above-mentioned contain a poisonous alkaloid.

6. Alcornin.—From the bark of *Alchornea latifolia*. The bark is exhausted, first with water and then with alcohol; the alcoholic liquid is evaporated; and the alcornin is taken up from the residue by ether, from which it crystallises (Blitz). The product is purified by recrystallisation from boiling alcohol, with the aid of animal charcoal (Frenzel).—Colourless silky needles, which sublime without decomposing. Neutral. Dissolves in hot fuming nitric acid, and is precipitated therefrom by water. Soluble with brown-yellow colour in oil of vitriol, from which it is thrown down by water, apparently unaltered, and with fine red colour in fuming sulphuric acid, without forming with it a conjugated compound (Frenzel, *N. Br. Arch.* 23, 173). It is not affected by weak acids, nor by ammonia or potash-ley, even when heated therewith. It is soluble in alcohol, from which it is precipitated by water; easily soluble in ether and cold oil of turpentine; nearly insoluble in cold, but easily soluble in hot oil of almonds and olive oil (Blitz, *Br. Arch.* 12, 46).

7. Alstonia bitter.—Obtained by precipitating a decoction of the bark of *Alstonia constricta*, one of the Australian *Apocynaceæ*, with

tannic acid. On drying the precipitate with oxide of lead, exhausting the residue with alcohol, and evaporating, the bitter remains as a dark-yellow amorphous mass, slightly soluble in ether and acids. Free from nitrogen (Palm, *Pharm. Viertelj.* 12, 161).

8. ANGELICA BITTER. — Occurs in that portion of the alcoholic extract which is soluble in water. The sugar which is present with it is first allowed to crystallise out; the malic and tannic acids are then precipitated with basic acetate of lead; the filtrate is freed from lead by hydrosulphuric acid and evaporated; and the residue is dissolved in alcohol. — The bitter thus obtained (which still contains sugar) is amorphous, yellowish, and translucent, easily soluble in water and alcohol, but insoluble in ether; it is not precipitated by ammonia, carbonate of soda, mercuric chloride, or tannic acid (Buchner, *Repert.* 76, 170). See also Buchholz & Brandes (*N. Tr.* 1, 2, 118).

9. ANGUSTURA BITTER. — Obtained by precipitating an aqueous solution of the alcoholic extract with basic acetate of lead, removing excess of lead by means of sulphuric acid, neutralising with ammonia, evaporating, and extracting the bitter with absolute alcohol. — Dark brown-red extract, very bitter, soluble in water and alcohol, insoluble in ether. It is precipitated by tannic acid, but not by basic acetate of lead, tartar emetic, or mercuric chloride (Winckler, *Repert.* 66, 336). See also Pfaff (*System der Materia medica*, 2, 45).

10. ANTIRRIN, ANTIRRACRIN. — From *Antirrhinum majus*. A decoction of the plant is precipitated with neutral and basic acetates of lead, filtered, freed from excess of lead, and precipitated with tannic acid. The latter precipitate is dissolved in alcohol and decomposed with oxide of lead, and the filtrate is digested with animal charcoal and evaporated, whereupon an amorphous residue is left, from which ether takes up antirracrin, leaving antirrin undissolved. *Antirracrin* is an amorphous body, of very pungent taste, soluble in alcohol and ether, insoluble in water. *Antirrin* forms yellowish-white scales, having a very bitter taste (Walz, *Jahrb. pr. Pharm.* 27, 74). *Linaria cymbalaria* contains similar substances (Walz, *Jahrb. pr. Pharm.* 27, 129).

11. The seeds of *Anthemis nobilis* contain, according to Bley (*N. Br. Arch.* 1, 76) a bitter substance, which is precipitated from the aqueous extract by animal charcoal, and may be extracted from the washed charcoal by alcohol. It forms a yellow, very bitter extract, destitute of alkaline properties.

12. BIRTHWORT BITTER. Walz's *Clematidin.* — From *Aristolochia Clematitis.* — 1. The plant is exhausted with ammonia-water; the extract is precipitated with neutral acetate of lead; the precipitate is triturated with alcohol and decomposed with dilute sulphuric acid; excess of the acid is removed by baryta-water; the filtrate is decolorised with animal charcoal and evaporated; and the residue is freed from resin by means of ether, and purified by dissolving it in ether and evaporating slowly (Walz, *Jahrb. pr. Pharm.* 26, 73). — Winckler *Jahrb. pr. Pharm.* 19, 71) precipitates the ammoniacal extract with dilute sulphuric acid [leaving most of the bitter in solution (Walz)], washes the resinous precipitate with cold water, in which it is insoluble,

dissolves it in 80 p. c. alcohol; decolorises the solution with animal charcoal; evaporates; and frees the residue from resin by repeatedly dissolving it in cold water and evaporating. Thus obtained, the bitter still contains salts. — Amorphous, golden-yellow mass, having a very bitter taste. Neutral. Contains 50·04 p. c. C., 4·90 H., and 45·06 O. (Walz). — When heated on platinum foil, it melts, evolves inflammable vapours, and leaves easily combustible charcoal. — It is coloured olive-green by oil of vitriol, and afterwards, on addition of water, deposits yellowish-white bitter flocks, soluble in alcohol. — It dissolves in nitric acid, forming a red-brown solution, from which water precipitates it in yellow flocks, apparently unaltered (Walz). — According to Winckler, it dissolves in water in all proportions; according to Walz, in 200 parts of cold, and 50 parts of boiling water, and much more freely in saline solutions. — It is insoluble in cold hydrochloric acid, and turns soft in the hot liquid. It dissolves in aqueous alkalis more freely than in water, forming brown solutions (Walz). The aqueous solution, after standing some time, precipitates tincture of iodine reddish-brown; iodic acid pale-yellow [with liberation of iodine (Winckler)]; ferric chloride yellow; sulphate of copper greenish-yellow; mercuric chloride yellow; bichloride of platinum and nitrate of silver yellowish-brown. It immediately throws down an abundance of yellow flocks from neutral and basic acetates of lead. The precipitate produced by an alcoholic solution of the bitter in neutral acetate of lead contains, on the average, 51·50 PbO., 24·25 C., 2·40 H., and 21·85 O. (Walz). — The bitter dissolves easily in alcohol, but not in ether, and is not precipitated by tannic acid (Walz; Winckler).

Serpentaria bitter, which, according to Winckler, is identical with birthwort bitter, is obtained from the roots of *Aristolochia Serpentaria*. — Chevallier precipitates the aqueous decoction with neutral acetate of lead; washes the precipitate with water, and boils it with alcohol, which dissolves bitter and resin; evaporates the solution; and extracts the bitter from the residue with water, the resin remaining undissolved. — Bitter and acrid; easily soluble in water and alcohol. The aqueous solution does not precipitate metallic salts, not even neutral acetate of lead, and it precipitates the basic acetate only after some minutes. The precipitation of the bitter by neutral acetate of lead in its preparation is due to the presence of phosphoric and malic acids (Chevallier, *J. Pharm.* 6, 565). Feneulle, on the contrary, separates the precipitate produced by neutral acetate of lead in a decoction of the root; frees the filtrate from lead by sulphuric acid; evaporates; and dissolves the residue in water and in alcohol alternately. The yellow, very bitter, hygroscopic mass thus obtained is precipitated from its aqueous solution by metallic salts and also by tincture of galls (Feneulle, *J. Chim. méd.* 2, 434).

Frickhinger's *Aristolochia yellow* and *Ariotolochia resin* are obtained from the year-old underground stems of *Aristolochia Clematitis*.

When the dried and powdered stems are exhausted with ether and the extract is evaporated, there remains a thick brown residue, in which crystals of aristolochia yellow form slowly and may be purified by washing with ether. — The crystals are also obtained by evaporating the aqueous extract to a syrup, agitating with ether, and evaporating the ethereal liqnid. — It forms amber-yellow transparent prisms, half a line in length, which melt and decompose when heated. After trituration, the crystals dissolve with golden-yellow colour in cold and hot water, and likewise in ammonia and alkalis, and are precipitated from all these solutions by acids. The aqueous solution gives a lemon-yellow precipitate with neutral and basic acetates of lead, and an orange-coloured precipitate with nitrate of silver. The yellow dissolves in alcohol and very easily in ether.

The *resin* is obtained by evaporating the mother-liquor from which the yellow has crystallised, treating the residue with alcohol, which leaves wax undissolved, and evaporating the alcoholic solution. It may be freed, though imperfectly, from yellow and bitter principle by boiling it with water. It is a soft body, of biting balsamic taste, soluble in ether and alcohol, insoluble in ammonia, soluble in potash-ley, and precipitated therefrom by acids. It is coloured a fine emerald-green by hydrochloric acid (Frickhinger, *Repert.* [3] 7, 12).

On an *acid resin* from the root of *Aristolochia grandiflora*, see Brandes (*Ann. Pharm.* 7, 287); on *soft resin* of *Radix Aristolochiæ antihysterica*, see Wittstein (*Repert.* 57, 152); on *resinous yellow* of the root of *Aristolochia Serpentaria*, see Feneulle (*J. Chim. méd*, 2, 431).

13. **Avornin**—Occurs in the bark of *Rhamnus Frangula*. See xvi, 71, *et seq*. A hot aqueous extract of the bark is evaporated to a syrup and mixed with an equal volume of 94 p. c. alcohol; the flocculent precipitate thereby produced is removed; and the filtrate is mixed with four times its volume of absolute alcohol, which throws down cathartic acid (p. 241). The filtrate is mixed with ether, and again filtered to separate a precipitate; the solution is evaporated; the residue treated with water, which leaves avornin undissolved; and the product is purified by dissolving it repeatedly in 50 p. c. alcohol and precipitating with water.—Brown mass, black after drying; dissolves in ammonia-water and precipitates metallic salts. Contains 57·08 to 58·38 p. c. C., 5·35 H., and in the silver-salt 60·81 p. c. AgO.—When boiled with strong hydrochloric acid, it yields 18·16 p. c. of sugar, together with yellow flocks which crystallise from ether, after addition of alcohol, in red flexible needles. The crystals melt at about 268°, sublime, dissolve in oil of vitriol with blood-red colour, and form with ammonia and the fixed alkalis, purple-red solutions which are precipitated by acids. These needles, Kubly's *avornic acid*, contain 64·07 p. c. C., 4·32 H.; in the insoluble lime-salt 12·2 p. c. of lime. Kubly gives the formulæ $C^{16}H^9O^8$ for avornin, $C^{16}H^7Ag^2O^8$ for avornin-silver, $C^{22}H^9O^8$ for avornic acid, and $C^{22}H^8CaO^8$ for the lime-salt (Kubly, *N. Repert.* 15, 295).

14. **Becuibin.**—Occurs in Becuiba juice, and in the fresh bark of *Myristica Bicuhyba* (see xvi, 396). When the sap which flows from the bark is mixed with water, the filtered extract evaporated, and the residue exhausted with ether and boiling alcohol in succession, the alcoholic tincture deposits brick-red granules of becuibin. The same granules are deposited more abundantly from a hot alcoholic solution of an aqueous extract of the fresh bark, on cooling. They are purified by washing with cold absolute alcohol and recrystallising from the boiling liquid.—Reddish glistening laminæ, inodorous, tasteless, slightly acid, and combustible. The substance dissolves in boiling water, but is insoluble in cold water and in caustic potash. It dissolves in ammonia, and is precipitated from the solution by acetic acid. It is

soluble in hot alcohol and in chloroform, but not in cold alcohol or ether (Peckolt, *N. Br. Arch.* 107, 158).

15. Caïlcedrin.

E. Caventou. *N. J. Pharm.* 16, 355; *Repert.* [3] 4, 397.—*N. J. Pharm.* 33, 123; *Pharm. Viertelj.* 8, 51.

The bitter principle of cailcedra bark, which is obtained from *Swietenia senegalensis.*

Preparation. An extract of the bark prepared with hot water is exhausted with alcohol; the tincture is precipitated with basic acetate of lead; the filtrate is concentrated, freed from lead by hydrosulphuric acid, and evaporated; and a solution of the residue in a small quantity of water is shaken with chloroform, which takes up caïlcedrin and leaves it behind on evaporation. The product is purified by precipitating its alcoholic solution with water.

Properties. Brittle, very bitter yellowish resin. Softens in hot water. Neutral. Contains 64·9 p. c. C., 7·6 H., and 27·5 O.

Caïlcedrin is nearly insoluble in *water*, but imparts its bitter taste to the liquid. The somewhat stronger solution in hot water fluoresces like sulphate of quinine.

It loses its bitterness almost entirely when boiled with *lime*, and apparently forms with lime and magnesia compounds which are soluble in water and alcohol.

The aqueous solution is precipitated only by *tannic acid*, the white precipitate dissolving in excess of the precipitant.

Dissolves easily in *alcohol*, *ether*, and *chloroform.*

16. Calendulin.—Obtained from the leaves and flowers of *Calendula officinalis*. An alcoholic extract of the plant is treated with water and ether, which leave the calendulin behind. Or an aqueous extract is exhausted, first with weak spirit, and afterwards with absolute alcohol; the wax which deposits from the latter liquid on cooling is separated; and the filtrate is evaporated. The calendulin thus obtained is freed from chlorophyll by ether.—Yellowish, transparent, friable mass, neutral, inodorous, and tasteless, swelling up to a transparent colourless jelly in water, without dissolving to any appreciable extent, even in the boiling liquid. According to Geiger, it yields by dry distillation an ammoniacal distillate, but, according to Gmelin, this is not the case. It is insoluble in dilute sulphuric and phosphoric acids, and in fuming hydrochloric acid. It dissolves in aqueous ammonia and potash, from which it is precipitated by acids; but is insoluble in aqueous carbonate of potash and lime-water. The alcoholic solution does not precipitate neutral acetate of lead or corrosive sublimate.—Calendulin dissolves easily in strong acetic acid, and in absolute and slightly hydrated alcohol. This last solution leaves the calendulin in pellicles when evaporated, and solidifies to a jelly when mixed with water. Calendulin is insoluble in ether and in volatile and fixed oils, and is not thrown down from its alcoholic solution by tincture of galls (Geiger,

Dissert. de Calendula officinali, Heidelberg, 1818; Stoltze, *Berl. Jahrb.* 1820).

17. Californin.. — The bitter principle of the bark of *China californica* (Wiggers, 126). See also Mettenheimer (*N. Jahrb. Pharm.* 1, 341). The bark is exhausted with ether and then boiled with 80 p. c. alcohol; the decoction is evaporated; the residue exhausted with water; and the solution precipitated with neutral acetate of lead. The filtrate freed from lead by means of sulphate of soda, is evaporated over the water-bath; the residue is exhausted with 90 p. c. alcohol; and the alcoholic solution is decolorised with animal charcoal, precipitated with ether, and left to stand for 24 hours, whereupon a concentrated solution of the bitter is found to be deposited. This is washed with ether and dissolved in water, and the solution is evaporated to dryness. — Pure golden-yellow, amorphous, friable mass, bitter and neutral. It is turned brownish-red by oil of vitriol. Dissolves in water and alcohol, but not in ether. Not precipitated by tannic acid, corrosive sublimate, or bichloride of platinum (Winckler, *Repert.* 82, 28; 89, 315; 91, 220).

18. Carapin. — Obtained from the bark of *Carapa guianensis*. An alcoholic extract of the bark is exhausted with water, and the solution is boiled with magnesia, whereby it is decolorised, without any vegetable base being thrown down by the magnesia. The filtrate is evaporated to a syrup, which is exhausted with alcohol; and the alcoholic liquid is concentrated and shaken with chloroform, which takes up carapin. The product is purified by agitating its alcoholic solution with animal charcoal. — Or, an aqueous extract of the bark is exhausted with alcohol; the tincture precipitated with basic acetate of lead; the filtrate evaporated; the residue dissolved in alcohol and treated with hydrosulphuric acid; and the solution filtered, digested with animal charcoal, and evaporated. The residual extract is treated with chloroform, which takes up carapin. — Pale-yellow shining varnish, bitter and neutral. Combustible. Contains 54·04 p.c. C., 6·54 H., 38·42 O., and traces of nitrogen. It is carbonised by oil of vitriol, but is not affected by other acids. Caustic potash-solution takes up from it a little yellow colouring matter. It is soluble in hot, but nearly insoluble in cold water, easily soluble in alcohol and chloroform, less freely in ether and bisulphide of carbon, and insoluble in oil of turpentine. The cold-saturated aqueous solution is rendered turbid by tannic acid (Caventou, *Pharm. Viertelj.* 10, 422). — A carapa bark different from the above was investigated by Petroz and Robinet (*J. Pharm.* 7, 351).

19. Cascarilla Bitter. — Obtained from cascarilla bark by exhausting the alcoholic extract with water, and evaporating. Dark honey-yellow, bitter and aromatic. Still contains ash (Trommsdorff, *N. Tr.* 26, 2, 142). — An aqueous infusion of the bark is precipitated with neutral acetate or lead; and the filtrate is freed from lead by hydrosulphuric acid, concentrated to one-third of its bulk, decolorised with animal charcoal, and evaporated to a syrup. The crystals which are deposited after standing for some time are digested with a small quantity of cold alcohol, which dissolves most of the colouring matter, and the undissolved portion is purified by recrystallisation from boiling alcohol with the help of animal charcoal. — White needles or hexagonal tables,

inodorous, bitter, neutral, and free from nitrogen. When heated, it melts to a brownish-yellow syrup, and afterwards solidifies in a resinous mass. It is combustible, and not volatile without decomposition. It forms with strong nitric acid a yellow solution, which is precipitated by ammonia. Oil of vitriol forms with it a dark-red solution, which is turned grass green and afterwards decolorised by water, with production of a green precipitate. It dissolves in strong hydrochloric acid with a violet colour, which is turned blue by a little water, and green by a larger quantity. — It is very slightly soluble in water, and is not precipitated from the solution by lead-salts or by tannic acid. Dissolves in alcohol and ether (Duval, *N. J. Pharm.* 8, 95).

20. CHENOPODIN. — Occurs in *Chenopodium album*, more abundantly in young than in mature plants. 1. The sap of the flowering plant is freed from albumin and chlorophyll by boiling, and evaporated; the residue is exhausted with alcohol; the tincture evaporated; and the remaining extract treated with absolute alcohol. This solution, on spontaneous evaporation, deposits chenopodin, which is to be washed with absolute alcohol and ether. — 2. On submitting the sap to dialysis in a Graham's dialyser, the walls of the vessel become covered with a viscid layer, which contains chenopodin. The deposit is dried and exhausted with alcohol; the tincture is evaporated; the residue boiled with water; and the decoction evaporated to a syrup, whereupon granules are deposited, which may be obtained in a purer state by digesting them in absolute alcohol, boiling, filtering, and setting aside the solution. — Yellowish-white, nearly inodorous granules, having a faint taste. Neutral. Under a magnifying power of 65 diameters it appears to consist of globules with rough surfaces, each of which exhibits in polarised light a black cross resembling that of calc-spar. The cross disappears on moistening with absolute alcohol, but reappears in a quarter of an hour. — When heated in a glass tube, it swells up, gives off water, an odour of burnt horn, a white vapour, and a sublimate of unchanged chenopodin. — Tincture of iodine produces in it a yellowish turbidity. — It is not affected by acids or alkalis. — It dissolves to a slight extent in water; more freely in weak spirit; and with difficulty in absolute alcohol and wood-spirit (Reinsch, *N. Jahrb. Pharm.* 20, 268; 21, 132; 23, 73). — Concerning a similar body, *Carviolin*, obtained from cauliflower, see Reinsch (*N. Jahrb. Pharm.* 26, 196).

From further experiments by Reinsch (*N. Jahrb. Pharm.* 27, 193; 28, 66, *Chem. Centr.* 1868, 32; *Jahresb.* 1867, 531) chenopodin, or rather *chenopodine*, appears to be an organic base having the composition $C^{12}NH^{13}O^{8}$, and to be likewise formed in the putrefaction of yeast and of plant-juices. It sublimes at about 160°—280°, melting at the same time and emitting a repulsive odour. It dissolves in 3 or 4 pts. of hot and in about 11 pts. of cold *water*, in 77 pts. of boiling and 200 pts. of cold *alcohol*. The alcoholic solution mixed with *bromine* deposits a red powder, and the supernatant solution contains a salt which crystallises in cubes. The *hydrochlorate* also crystallises in cubes; the *sulphate* and *nitrate* in rhombic needles. The concentrated hydrochloric acid solution is precipitated by platinic chloride.

21. CHIMAPHILIN. — Occurs in *Pyrola umbellata*. — An extract of the plant prepared with weak spirit is shaken with chloroform; the upper

layer of liquid is decanted and the lower is left to evaporate spontaneously. The crystals thereby formed are recrystallised from alcohol. — On distilling the plant with water, the chimaphilin passes over and solidifies in the neck of the retort. — Golden-yellow needles, sometimes 1½ inch long, without odour or taste. Fusible and susceptible of sublimation. — Carbonised by oil of vitriol, but not affected by concentrated nitric or hydrochloric acid. — Nearly insoluble in water. Not precipitated from alcoholic solution by corrosive sublimate or tannic acid. Soluble in alcohol, ether, chloroform, and in volatile and fixed oils (Fairbank, *Pharm. Viertelj.* 9, 582).

22. Bitter principle of China bicolor. — The bark is first treated with ether, and afterwards exhausted with alcohol; the tincture is evaporated; and the residue treated with water, which leaves resin undissolved. The aqueous solution is mixed with a little phosphoric acid, digested with animal charcoal, filtered and evaporated; and the product is purified by solution in absolute alcohol and in water. — Pale-yellow, very bitter. It is carbonised by oil of vitriol, and yields traces of oxalic acid by the action of strong nitric acid. The aqueous solution is not affected by acids and alkalis, and does not precipitate metallic salts, with the exception of basic acetate of lead (Pelletier & Petroz, *J. Pharm.* 11, 453). Vauquelin (*J. Pharm.* 11, 456) obtained precipitates also with tartar-emetic, ferrous sulphate, terchloride of gold, and infusion of galls.

23. Cornin or Cornic Acid. — The bitter principle of the root-bark of *Cornus florida*. Discovered by Geiger. Carpenter's alkaline cornine (*Mag. Pharm.* 15, 146), which Tromsdorff was unable to find (*Br. Arch.* 25, 59), is, according to Geiger, a mixture of lime-salts and the bitter principle.

The bark of the root is exhausted with cold water; the infusion is shaken with freshly precipitated hydrate of lead; and the filtrate is evaporated to an extract, which is exhausted, first with a mixture of alcohol and ether, and then with absolute alcohol. The extract left by the evaporation of the ether-alcohol solution, when dissolved in absolute alcohol, mixed with ether till turbidity is produced, filtered, and evaporated, yields crystalline scales of cornin.

Stellate groups of delicate, satiny, white needles, having a very bitter taste. — When heated, it melts easily, blackens, emits white non-ammoniacal vapours, and burns with luminous flame, leaving charcoal. On fusing it with hydrate of potash, a little ammonia seems to be produced.

Cornin dissolves very easily in water. The aqueous solution is rendered darker by alkalis without being precipitated, and is not affected by tincture of iodine, chloride of barium, neutral acetate of lead, ferric chloride, corrosive sublimate, or tincture of galls. It gives a granular precipitate with basic acetate of lead, and partly loses its bitterness when treated with hydrate of lead. — Nitrate of silver produces a white crystalline precipitate, which is not affected by exposure to light for 24 hours, nor by heating, and dissolves completely in nitric acid after addition of water only.

Cornin dissolves easily in alcohol and with difficulty in ether, in which the impure substance is insoluble (Geiger, *Ann. Pharm.* 14, 206). See, also, Cockburn (*Ann. J. Pharm.* 7, 109), and Maisch *Chem. News* 4, 198; *Kopp's Jahresber.* 1861, 766).

Resin from Cornus florida.—The bark, previously treated with water, is exhausted with alcohol; the tincture is freed from tannic acid by agitation with hydrate of lead; and the filtrate is concentrated, whereupon a yellowish-white granular powder is deposited. This, after washing with water, crystallises from alcoholic solution, by spontaneous evaporation, in shining laminæ, and from ethereal solution in granules. Inodorous and tasteless. Neutral.

The resin melts when heated, evolves white clouds having an empyreumatic resin-like odour, and afterwards burns with luminous smoky flame.—It becomes slightly coloured in cold nitric acid, and dissolves completely in the hot acid, emitting a small quantity of red fumes: the solution deposits a white powder on cooling, and when mixed with water, throws down bulky white flocks of the apparently unaltered substance.—Oil of vitriol dissolves it, forming a yellowish-red solution, which turns black on the addition of a little water, and is decolorised by more water, with precipitation of white flocks.—When heated with solid hydrate of potash, it is carbonised, without evolving ammonia.

It dissolves to a very slight extent in boiling water, but not in hydrochloric acid, or boiling strong potash-ley.—The alcoholic solution is not precipitated by metallic salts.—It dissolves in cold, and more freely in hot, strong acetic acid, from which it is precipitated by water; with difficulty in cold, more easily in hot alcohol; and very easily in ether (Geiger).

24. Cratægin.—Occurs in the fresh bark of the young twigs of *Cratægus oxyacantha*. An aqueous decoction of the bark is treated with hydrate of lime; the filtrate is reduced to a syrup and mixed with alcohol, to throw down gum and salts; and the filtrate is evaporated to crystallisation.—Very bitter, greyish warts. Neutral. Burns with emission of an aromatic odour. Easily soluble in water, less easily in alcohol of 38°, and insoluble in ether, which precipitates it from the alcoholic solution. It does not combine with acids or alkalis.—When a decoction of the bark is precipitated with basic acetate of lead, the filtrate freed from lead and evaporated, and the residual brown extract purified by dissolving it in water and precipitating with alcohol, long white needles are obtained, having a faintly bitter taste, soluble in water and alcohol, but not in ether, and differing from cratægin (Leroy, *J. Chim. méd.* 17, 3; *N. Br. Arch.* 28, 209). Probably mannite? (Kr).

25. Crepin. From *Crepis fœtida*. A tincture of the dried flowering plant is precipitated with basic acetate of lead and filtered, and the filtrate is freed from excess of lead by hydrosulphuric acid and evaporated. The brown, very bitter residue is treated with ether, which takes up crepin, and leaves it in crystals on evaporation (Walz, *N. Jahrb. Pharm.* 13, 176).

Crotonin.—Concerning the crotonin of Brandes, see *Handbuch*, viii, 23.

26. Cusparin or Angustura Bitter.—Occurs in true Angustura bark. A tincture, prepared with 1 part of the bark and 3 parts of cold alcohol of sp. gr. 0·795, deposits, when slowly evaporated, crystalline nodules, which are to be washed with a little water and alcohol, shaken

with hydrate of lead, and freed from fat and colouring matter by ether. — Four-sided needles, arranged in tufts. Neutral. Melts at 45°, gives off 23·1 p. c. of water at a higher temperature, and decomposes at 133°. Very bitter and somewhat biting, not poisonous; free from nitrogen. — It is turned greenish-yellow by cold nitric acid, and brown-red by oil of vitriol, but is not coloured by iodic and hydrochloric acids. 100 parts of water at 15° dissolve 0·545 parts, at 60° 0·717 parts, and at 100°, 1·104 parts of cusparin. — It dissolves easily in acids, and without decomposition in alkalis. Its solutions do not precipitate metallic salts; they are coloured purple-red by mercurous nitrate, and yield an abundant precipitate with tincture of galls. It is soluble in alcohol, but not in ether or volatile oils (Saladin, *J. Chim. méd.* 9, 388).

27. DIGITALIN (xvi, 330).

¶ Nativelle (*J. Pharm.* [5], 9, 255) prepares crystallised digitalin by mixing 100 pts. of coarse digitalis powder with a solution of 25 pts. neutral lead acetate in 100 pts. water, and exhausting with water after 12 hours. The residue is treated with alcohol of 50 p. c., till the solutions become tasteless; the extract is mixed with a solution of 4 pts. lead acetate; the liquid is filtered; the decolorised solution is mixed with 2 pts. phosphate of soda, and again filtered; and the alcohol is distilled from the filtrate in the water-bath. The residue of the distillation contains small suspended crystals, surrounded by a yellow, very bitter substance. The whole is evaporated on the water-bath to about 10 pts.; the liquid is filtered off; the residue, after washing with cold water and pressing between paper, is dissolved in twice its weight of warm alcohol of 60 p. c.; and the solution is left to stand in a cold place. It then deposits, first crystals of an inactive substance, and after some days, radiate yellow crystals of digitalin. These are recrystallised from alcohol of 80 p. c., with addition of animal charcoal, and the dried and pulverised crystals are briskly shaken with 20 pts. of pure chloroform, which dissolves only the digitalin, leaving the foreign inactive substance behind. After the removal of the chloroform by distillation, there remains coloured digitalin, which may be purified by repeated crystallisation from alcohol, and boiling with animal charcoal.

Crystallised digitalin is neutral, inodorous, and has a very persistent, bitter taste. It is free from nitrogen.

			Nativelle.
50 C	300	51·73	51·33
40 H	40	6·89	6·85
30 O	240	41·38	41·82
$C^{50}H^{30}O^{30}$	580	100·00	100·00

It dissolves in all proportions of *chloroform*, in about 12 pts. of *alcohol* of 90 p. c. at ordinary temperatures, more easily at the boiling heat, less easily in absolute alcohol, and scarcely at all in alcohol containing ether. *Sulphuric acid* dissolves it with green colour, changed to currant-red by *bromine*-vapour, but recovering its green tint on addition of water. With *hydrochloric acid* it forms a green solution, from which water precipitates a resin (Nativelle).

On crystallised digitalin see also Lefort (*J. Pharm.* [5], 6, 424), who attributes the variations in the properties and physiological action of digitalin to the existence of two modifications, namely, the so-called German, or soluble digitalin, obtained from the seeds, and the insoluble from the leaves of the fox-glove, in which it exists in predominating quantity, together with a small quantity of the soluble variety.

The insoluble substance, mixed at first with the crystallised digitalin, is easily obtained pure by recrystallisation from alcohol. It then forms splendid colourless needles, perfectly tasteless, neutral, and free from nitrogen; less soluble in alcohol than digitalin; nearly insoluble in ether, chloroform, and water. Sulphuric acid dissolves it with currant-red colour, changing to yellow on addition of colour. Nitric acid dissolves it without colour; hydrochloric acid partially (Nativelle). ¶

28. Erythrocentaurin.

Mehu. *N. J. Pharm.* [4], 3, 265; abstr. *Pharm. Viertelj.* 12, 557; *Krit. Zeitschr.* 9, 336.

Occurs in *Erythræa Centaurium.*

Preparation. An aqueous extract of the flowering plant is exhausted with alcohol; the tincture is evaporated; and the residue is shaken repeatedly with ether. The yellowish-brown liquid which remains on distilling off the ether yields crystals by spontaneous evaporation, which are purified by pressing and recrystallising from boiling water, with the help of animal charcoal and carbonate of baryta. The product can be obtained colourless only by digesting an ethereal solution with 20 parts of animal charcoal for 14 days and evaporating. The dry plant yields $\frac{1}{3000}$th of erythrocentaurin.

Properties. Large crystals, without odour or taste. Neutral; optically inactive. Melts at 136°, and solidifies in a crystalline mass on cooling.

On exposure to direct sunshine, the colourless crystals quickly acquire a rose tint, changing to brilliant red, without alteration of weight. Solutions of the substance in ether or chloroform, when evaporated in sunlight, likewise deposit crystals coloured red internally. This change is produced only by the most highly refrangible rays of the spectrum; it is prevented when the light is made to pass through yellow or green glass, through chlorine gas, through nitrate of nickel, or through solutions of æsculin or sulphate of quinine. Bromine and iodine vapours, nitrate of uranium, and ammoniacal solution of nitrate of copper, on the other hand, do not absorb the colouring rays, which are stopped, however, by solutions of bromine or iodine in bisulphide of carbon, benzene, or alcohol.—The red crystals become perfectly colourless at 130°, and melt like the colourless crystals at 136°; they also yield perfectly colourless solutions, from which colourless erythrocentaurin crystallises in the dark.—Coloration and decoloration take place not only in air, but also when the air is displaced by hydrosulphuric acid, sulphurous acid, carbonic acid, and other gases.

			Mehu. *mean.*
54 C	324	68·06	67·66
24 H	24	5·04	5·09
16 O	128	26·90	27·25
$C^{54}H^{24}O^{16}$	476	100·00	100·00

Erythrocentaurin dissolves in 1,630 parts of *water* at 15°, and in about 35 parts of boiling water.—It dissolves freely and without coloration in *oil of vitriol*, from which it is thrown down unaltered by water.—It is not affected by fuming *nitric acid*, or by *hydrochloric acid*, *chromic acid*, or *peroxide of lead*, and does not combine with *alkalis*. It is not acted upon by *bromine* or *iodine*, even when these bodies are evaporated with it; but when it is melted in a current of *chlorine*, a viscid mass is obtained, an ethereal solution of which yields crystals, differing from erythrocentaurin, and not turning red on exposure to light. Erythrocentaurin is decomposed by *permanganate of potash* in the cold.—It is not affected, and not precipitated from solution, by *metallic salts* or *tannic acid*.

It dissolves in 13·5 parts of *chloroform*; in 48 parts of 86 p. c. *alcohol* at 15°; in 245 parts of *ether;* and easily in *bisulphide of carbon*, *benzol*, and *volatile* and *fixed oils*.

29. **Esenbeckin.**—Occurs in *Cortex Esenbeckiæ febrifugæ*.—Buchner (*Repert.* 31, 383, and 81, 63), from his own and from Nees von Esenbeck's experiments (*Repert.* 37, 1), inferred that this bitter differed from chinovin, and Winckler afterwards showed that the bark contains chinovin and two other bitter principles.—Winckler (*Repert.* 91, 314) evaporates the alcoholic tincture of an ethereal extract of the bark, and takes up the chinovin from the residue by ammoniacal water, which leaves esenbeckin as a white powder resembling magnesia, neutral, intensely bitter, and not crystallisable from alcohol or ether.

Second bitter from Cortex Esenbeckiæ. The bark previously exhausted with ether is treated with 80 p. c. alcohol; the tincture is evaporated; the residue digested with moderately strong solution of sulphate of soda; the solution is concentrated and shaken repeatedly with ether; the ethereal layer is decanted; the aqueous liquid evaporated to dryness; and the residue is dissolved in 90 p. c. alcohol. This solution is precipitated with basic acetate of lead, and the filtrate decolorised with animal charcoal and evaporated, whereupon there is left a hygroscopic pale-yellow extract, triturable to a white powder, soluble in alcohol and in water, but not in ether. When a solution of this body in a small quantity of alcohol is mixed with ether, a brownish-yellow syrup is deposited, which afterwards crystallises. The crystals, washed with ether-alcohol, form colourless, shining, intensely bitter scales, which undergo decomposition when heated. Neutral. Without action on tannic acid or metallic salts (Winckler).

30. **Feuillin.**—Obtained from the seeds of *Feuilla cordifolia*, a Brazilian plant. The seeds, freed from fat oil by expression, are boiled with alcohol; the tincture is evaporated, and the residue treated with boiling water so long as it continues to give up bitter substance. After cooling, the liquid is filtered and precipitated with basic acetate of lead,

then again filtered and precipitated with the neutral acetate. The latter precipitate is washed, and boiled with alcohol of sp. gr. 0·86; and the hot solution is freed from lead by hydrosulphuric acid, and evaporated to dryness. The residue is purified by dissolving it in boiling water and in absolute alcohol.—Amorphous, brown mass, neutral, inodorous, very bitter and acrid. Combustible. When boiled with dilute acids it yields no sugar. Its solution in hydrochloric acid, which is colourless at first, turns green on standing, and changes to rose-red when boiled, with deposition of green flocks.—It dissolves in warm water; easily in ammonia, from which it is precipitated by acids; and with difficulty in caustic potash. The aqueous solution is precipitated by many metallic salts, and by bichloride of platinum and tannic acid. It is easily soluble in absolute alcohol, but insoluble in ether and in chloroform.—The seeds contain, besides feuillin, a base, crystallising in colourless tables, which may be obtained from the filtrate of the lead precipitates. This body has an alkaline reaction, volatilises when heated on platinum foil, and gives a pale-yellow precipitate with bichloride of platinum (Peckolt, *N. Br. Arch.* 109, 219).

31. Ficarin. Occurs in the roots, in the tubers, and in traces in the leaves, of *Ficaria ranunculoïdes*. It is taken up from the aqueous extract by alcohol, and from the alcoholic extract by water. Closely resembles saponin. It is not coloured by ferric nitrate (St. Martin, *Répert. Chim. appl.* 1, 425; *Kopp's Jahresber.* 1859, 564).

32. Bitter from the bark of Galipæa officinalis.—A decoction of the bark is precipitated with basic acetate of lead, filtered, freed from lead by hydrosulphuric acid, boiled with animal charcoal, and evaporated to an extract. This is dissolved in alcohol, the solution evaporated, the residue dissolved in water, and the solution again treated with animal charcoal and evaporated.—Red-brown, amorphous, deliquescent, very bitter mass, easily soluble in water. Forms red solutions with hydrochloric and nitric acids, and a violet-red solution with oil of vitriol. Not precipitated by metallic salts or by tannic acid, and does not neutralise acids. Dissolves in alcohol, but not in ether (Husband, *J. Chim. méd.* 10, 334).

33. Gaultherin.—Obtained from the bark of *Betula lenta*, which when distilled with water yields oil of gaultheria (xii, 255), or a very similar oil, but does not contain it already formed.—An alcoholic extract of the bark is dissolved in water and digested with hydrate of lead; the filtrate is evaporated to dryness; the residue treated with alcohol; and the solution again evaporated.—The residual amorphous gummy mass yields by dry distillation empyreumatic products and oil of gaultheria. The same oil is obtained by distilling the mass with dilute hydrochloric or sulphuric acid. Fuming nitric acid produces yellow crystals precipitable by water. On boiling gaultherin with dilute nitric acid, yellow needles soluble in alcohol distil over. On boiling it with baryta-water, removing the baryta, neutralising with carbonate of lead, decomposing the soluble lead-salt thereby produced with hydrosulphuric acid, and evaporating, crystals of Procter's *gaultheric acid* are obtained, which dissolve easily in alcohol, and with difficulty in ether. They form amorphous salts, and yield gaultheria oil when

distilled with dilute sulphuric acid (Procter, *Pharm. Centr.* 1844, 473; *Berzel. Jahresber.* 25, 613).

34. Geraniin. — Occurs in the roots of various species of *Geranium*. An alcoholic tincture of the roots is freed from tannic acid by lime and evaporated, and the residue is treated with water. The yellow bitter extract taken up by the water is geraniin, insoluble in absolute alcohol and ether (Muller, *N. Br. Arch.* 22, 29).

35. Geum bitter. From *Radix Gei urbani.* The powdered root is mixed with one-third of its weight of hydrate of lime, and exhausted with 40 p. c. alcohol; the alcohol is distilled off; the residue is evaporated to dryness, and again exhausted with warm alcohol of sp. gr. 0·833; the tincture is evaporated to dryness; and the residue dissolved in water. This solution is freed from lime by means of oxalic acid, neutralised with carbonate of lead, filtered, and evaporated; and the residue is dissolved in alcohol, treated with hydrosulphuric acid, and evaporated to dryness, without filtering from the sulphide of lead. From the residue thus left the geum bitter is taken up by alcohol. — Amorphous honey-yellow extract, neutral and free from nitrogen. It is reddened by oil of vitriol, and converted into a yellow colouring matter by warm nitric acid. It dissolves with difficulty in water, and combines with potash, lime, and lead-oxide, to form compounds which are soluble in alcohol and in water, and are precipitated by acids. The lime-compound with excess of the bitter, gelatinises on cooling its solution in warm alcohol. — The bitter dissolves easily in alcohol and ether (Buchner, *Repert.* 85, 184; *Berzel. Jahresber.* 25, 718).

36. Granatin. — Obtained from the husks of unripe pomegranates. An alcoholic extract of the husks is freed from tannic acid and exhausted with dilute sulphuric acid, and the solution is precipitated with an alkali. An alcoholic solution of this precipitate yields crystals which burn when heated, emitting a bread-like odour, dissolve in dilute acids, and assume a blood-red colour in nitric acid (Landerer, *Repert.* 68, 363).

To this place belongs probably Latour de Trie's *sparingly soluble resin of the bark of pomegranate root* [his granatin is identical with mannite (xv, 356)], which is deposited from ethereal extracts of the bark on distilling off the ether, and is also precipitated from alcoholic extracts by water. It is a tasteless, yellowish-white, combustible powder, blackened by nitric acid, afterwards assuming a fine blood-red colour, and yielding oxalic acid when heated. Gives a yellow solution with oil of vitriol, is insoluble in water, sparingly soluble in ammonia, but freely soluble in alkalis, forming purple-red solutions which are precipitated by acids. Dissolves to a slight extent in ether and cold alcohol, and more freely in hot alcohol (Latour de Trie, *J. Pharm.* 17, 509).

Landerer (*Repert.* 61, 92) obtained from the bark of the wild pomegranate tree, crystals apparently different from granatin. They were obtained from an alcoholic tincture of the aqueous extract of the bark. White, silky, stellate groups of needles, having a pungent, peppery taste, and partially susceptible of sublimation; the sublimate, however, tastes sickly and sweetish. The crystals dissolve in 200 parts of water, in nitric acid with greenish-yellow colour, and in aqueous ammonia and alkalis (Landerer). — Righini's *punicin* is obtained from the same bark. On warming an alcoholic extract of the bark with potash-ley, and then dropping in sulphuric acid, an oleo-resinous mass is deposited, which solidifies at − 7°. It is yellowish-white, smells like veratrin, and has a pungent taste. Burns like a resin, emitting pungent vapours. Dissolves in acids, and is precipitated therefrom by ammonia (!) (Righini, *N. J Pharm.* 5, 298 ; *J. Chim. méd.* 20, 132).

37. Greenhartin. — Obtained by de Vrij from the greenheart wood of Surinam in the same way as bebirine (xvii, 170) is obtained from the wood of the bebeeru tree. According to Stein it is probably identical with taigutic acid (xvi, 521).

It crystallises from water in oblique prisms, and from alcohol in coherent shining golden crystals, resembling iodide of lead. It is easily fusible, and solidifies in a crystalline state on cooling ; sublimes partly in crystals. Tasteless in itself; bitter in alcoholic solution; contains, on the average, 74·64 p.c. C., and 5·32 H., corresponding to the formula $C^{60}H^{26}O^{12}$ (by calc. 74·6 p.c. C., 5·3 H.).

Greenhartin dissolves in warm nitric acid with brown colour, without liberating nitrous fumes. From a solution in boiling nitric acid water throws down yellow crystalline granules, which form chloropicrin with chloride of lime. — Chloride of lime decolorises the alcoholic solution. — Bromine evolves hydrobromic acid and forms an orange-coloured mass. On adding to the substance a saturated solution of bromine-water so long as the colour is destroyed, a bromine-compound is formed which is decomposible at 100°, nearly insoluble in water, easily soluble in alcohol with brown-red colour, easily also in soda-ley. After drying in a vacuum, it contains 42·61 p. c. C., 3·70 H., and 37·46 Br., corresponding to the formula $C^{60}H^{22}Br^{4}O^{12} + 6HO$. — Greenhartin boiled for 8 hours with baryta-water, evolves an aromatic odour, and yields formic acid and a distillate, which reduces nitrate of silver; but only a part of the greenhartin is decomposed.

Greenhartin is insoluble in cold water. The brownish-red solution obtained by prolonged boiling with water, deposits crystals after standing for some days, but it still remains coloured. — It dissolves in oil of vitriol with yellowish-red colour. — Ammonia, caustic alkalis, and baryta-water colour the crystals and the alcoholic solution dark-red, and form hair-like crystals. — Acetate of alumina colours the solutions purple; neutral and basic acetates of lead and acetate of copper act in a similar manner, but at the same time throw down precipitates. — Greenhartin does not reduce alkaline solutions of cupric oxide, even after boiling with acids. — It colours ferric chloride blood-red.

Dissolves in bisulphide of carbon, chloroform, alcohol, and ether, forming solutions which are golden-yellow in the cold, and brown-red in the boiling liquids (Stein, *J. pr. Chem.* 99. 1).

38. Guacin.—Occurs in the leaves of *Micania Guaco.* The leaves are exhausted with ether ; the tincture is distilled ; and the dry residue is boiled with water so long as it communicates thereto a bitter taste. The aqueous liquid is evaporated, and the remaining extract is dissolved in absolute alcohol and again evaporated. — Pale-brown, friable mass, inodorous, bitter, and not alkaline. Melts at 100°. Dissolves to a slight extent in cold water, and is deposited from its solution in boiling water on cooling. Dissolves in alcohol and ether (Fauré, *J. Pharm.*

22, 291). M. Pettenkofer (*Repert.* 86, 311) exhausts the leaves with alcohol, decolorises the tincture with animal charcoal, which does not remove the bitter taste, distils, dissolves the residue in ether, and evaporates the solution. The pale-brown brittle resinous guacin is partially soluble in water. In the moist state, or when treated with dilute sulphuric acid, it emits the stupefying odour of the fresh leaves. Doses of 1 grain produce vomiting.

39. Hop-bitter. — Prepared pure and investigated by Lermer. Payen & Chevallier (*J. Pharm.* 8, 216; *J. Chim. méd.* 2, 533) distinguish a bitter principle (*Lupulite*), and a resin of hops. The latter, according to Vlaanderen (*Scheikund. Verhandel. en Onderzoek* II, *Deel* 1, *Stuck. Onderz.* 87; abstr. *Kopp's Jahresber.* 1858, 448), is dark-brown and inodorous, and has the composition represented by the formula $C^{54}H^{35}O^{11}$. — According to Wagner and Fluckiger (*Pharm. Viertelj.* 14, 7) hops contain quercitrin (xvi, 496), which is denied by Lermer. On an acrid soft resin from the shoots of the hop, see Leroy (*J. Chim. méd.* 16, 3).

Preparation. Fifteen pounds of hops are exhausted with sixty pounds of ether; the ether is distilled off; and the blackish-green soft residue is treated with cold alcohol, which leaves wax undissolved. The liquid is filtered and evaporated, and the residue again dissolved in ether. The ethereal solution, shaken repeatedly with strong potash-ley, so long as it imparts thereto a yellow colour, gives up resins, a portion of the bitter, and other substances. The supernatant brown ethereal layer contains a compound of hop-bitter with potash, which is dissolved out by agitation with water. The aqueous solution is precipitated with cupric sulphate; the precipitate is collected (together with more of the same compound which crystallises from the filtrate on spontaneous evaporation), carefully washed with not too large a quantity of ether, dissolved in more ether, and decomposed with hydrosulphuric acid. The solution, filtered from sulphide of copper, is evaporated in a current of carbonic acid to a syrup, which on standing for 24 hours or longer, solidifies to a brown mass of crystals. This must be freed from the mother-liquor by triturating it with nitrobenzene, and placing it on dry plates of plaster of Paris, as other liquids dissolve both the mother-liquor and the crystals (Lermer).

Lermer noticed also the following bodies:—*a.* Fine white needles, melting above 110°, contained in the potash-ley with which the ethereal solution is shaken in the above process. They are obtained therefrom by adding sulphuric acid till turbidity is produced, precipitating with cupric sulphate, decomposing the dirty-yellow precipitate with hydrosulphuric acid, dissolving in ether, and recrystallising from the same liquid. — *b.* Reed-like microscopic crystals, which sublime with partial decomposition when heated, and probably contain nitrogen. They remain dissolved in the ether after the separation of the potash-compound of hop-bitter by water (see above), and are deposited, on evaporation, in the form of a grey soft mass which crystallises from ether.

Properties. Brittle, highly lustrous, rhombic prisms, having an acid reaction. Tasteless in itself, but intensely bitter in alcoholic solution. When kept (in the air ?) it turns yellow, soft, and uncrystallisable.

Hop-bitter is insoluble in *water*. — Its *copper compound* (see above) is a deep blue precipitate, which is paler after drying, and is also obtained in crystals soluble in a large quantity of ether; contains, on the average, 60·79 p. c. C., 7·29 H., 19·22 O., and 12·70 CuO., corresponding to the formula $C^{32}H^{25}O^{7},CuO$ (calc. 61·4 p. c. C., 7·99 H., 12·7 CuO).

The bitter dissolves very easily in *bisulphide of carbon*, *alcohol*, *ether*, *chloroform*, *benzol*, and *oil of turpentine*. (Lermer, *Dingl.* 169, 54; *Pharm. Viertelj.* 12, 504; *Kopp's Jahresber.* 1863, 598.)

40. Poisonous substance from the husks of Hyænanche globosa, a South African plant of the euphorbiaceous order. An aqueous decoction of the husks is precipitated with neutral acetate of lead; the filtrate is treated with hydrosulphuric acid, again filtered, and evaporated; and a strong aqueous solution of the residue is mixed with alcohol, which throws down gum and salts of malic acid. The filtrate, mixed with ether, deposits sugar as syrup, after which the decanted ethereal solution, when evaporated, leaves the poison in the form of a yellow varnish, still containing small quantities of acetic acid and volatile oil. Amorphous, very bitter; fatal in small doses. Dissolves easily in water (Henkel, *N. Br. Arch.* 94, 30).

41. Bitter of Iceland Moss. — An extract of the lichen prepared with hot alcohol is freed from sugar and salts by treating it with warm water, and from leaf-green by means of a little alcohol, whereupon the bitter is left as a pale-yellow, light, very bitter powder. It dissolves sparingly in cold, more easily in hot water, easily in aqueous carbonates of the alkalies, forming a green very bitter liquid, which loses its bitter taste when boiled, the aqueous solution depositing at the same time a brown powder. Hydrochloric and acetic acids throw down from the alkaline solution, white flocks soluble in excess of acid. Basic acetate of lead and mercurous nitrate precipitate the aqueous solution. — The bitter dissolves somewhat more freely in alcohol than in water, forming a yellowish-green solution (Berzelius, *Schw.* 7, 332).

42. Kaempferide. — Obtained from Galanga root. The coarsely powdered root is exhausted with ether, and the tincture is distilled, whereupon a brown viscid balsam, interspersed with crystals, is left behind. The crystals are isolated, though with difficulty, by oft-repeated treatment of the residue with weak alcohol, strong alcohol, and ether, in succession. When heated in a water-bath, they yield an oil, after the removal of which they are to be recrystallised from alcohol. Yellowish, pearly laminæ, neutral, inodorous, tasteless, and not fusible at 100°. Combustible. Oil of vitriol colours the substance yellow, changing to dark green, after which water throws down a brown resin. — Dissolves in 1,000 pts. of boiling water; in ammonia and caustic potash with deep yellow colour; and in carbonate of soda with liberation of carbonic acid, the solution forming a jelly when cold. It is soluble also in hot acetic acid; in 50 pts. of 75 p. c. alcohol; in 6 pts. of boiling ether, and in 25 pts. of ether at 18°. Contains, on the average, 64·48 p. c. C., 4·40 H., and 31·12 O. (Brandes, *N. Br. Arch.* 19 52.)

43. Bitter principle of Copalche bark. Nauseous bitter extract, contained in that portion of the alcoholic extract which is soluble

in water and not precipitable by basic acetate of lead. The aqueous solution assumes a rose colour with oil of vitriol. It is precipitated by stannous chloride, ferrous sulphate, and infusion of galls (Mercadieu, *J. Chim. méd.*, 1, 236).

44. BITTER PRINCIPLE OF LATHYRUS ANGUSTIFOLIUS. — Obtained by treating an alcoholic extract of the seeds with ether, dissolving the residue in 94 p. c. alcohol containing ether, and evaporating. — Yellowish, soft, very bitter mass, which, after boiling its aqueous solution with animal charcoal and evaporating the filtrate, appears of a faint yellow colour, whilst the charcoal is found to have taken up a brown bitter substance. — Neutral. Burns with a feebly luminous flame. Carbonises in a platinum spoon, emitting an odour of acetic acid. Its concentrated solution is coloured brown by oil of vitriol; a dilute solution is not affected thereby. It is precipitated by tincture of galls (Reinsch, *Jahrb. pr. Pharm.* 18, 37).

45. LINARIN. LINARACRIN. LINARESIN. — Obtained from *Linaria vulgaris*. When a decoction of the plant is freed from matters precipitable by basic and neutral acetates of lead and from excess of lead, and is then mixed with tannic acid, a precipitate is formed which contains the three above-mentioned substances. This precipitate is decomposed by oxide of lead, and its constituents are separated by treatment with alcohol, ether, and water. — *Linarin* is white, crystalline, bitter, soluble in water. *Linaracrin* is a yellowish-brown, amorphous, acrid resin, soluble in ether. *Linaresin* is yellowish-brown, friable, slightly acrid, soluble in alcohol, but not in water or ether (Walz, *Jahrb. pr. Pharm.* 27, 16).

46. LININ.

PAGENSTECHER. *Repert.* 72, 311; further with corrections, 76, 213, and 79, 216.
L. A. BUCHNER. *Repert.* 88, 173.
C. SCHRÖDER. *N. Repert.* 10, 11; *Chem. Centr.* 1861, 124; *Kopp's Jahresber.* 1860, 546.

Occurs in *Linum catharticum* (*Handbuch*, vii, 29), especially after flowering.

Preparation. 1. The plant is digested with thin milk of lime; the bright yellow filtrate is mixed with hydrochloric acid and shaken with ether; and the ethereal layer is decanted and submitted to distillation, whereupon linin crystallises from the residue (Schröder). — 2. An aqueous extract of the plant is treated with alcohol; the tincture is distilled, and the residual liquid is left at rest for some days; it then deposits a friable resin containing linin. This is washed with water, and then with ether or cold alcohol of sp. gr. 0·88, which dissolves the resin and leaves white linin; crystallisable by spontaneous evaporation of its solution in absolute alcohol (Pagenstecher). — 3. The dried plant is exhausted with absolute alcohol; the tinctures are evaporated; the residue is treated with water, and the remaining undissolved portion with strong acetic acid, which dissolves linin, leaving resin and chlorophyll behind. The acetic solution when mixed with water deposits linin, which is washed by decantation, and may be obtained perfectly white by repeated solution in warm 20 to 30 p. c. alcohol. — Impure linin may also be purified, either by mixing it with alcoholic neutral acetate of lead and ammonia, evaporating to dryness, and extracting the linin from the pulverised residue by ether; or by triturating its alcoholic solution to a pulp with commercial carbonate of soda, and shaking with ether, which takes up the linin (Pagenstecher). — 4. Buchner frees an aqueous extract of the plant from albumin by boiling and filtration; adds to it a sufficient quantity of hydrochloric or sulphuric acid; collects the resulting precipitate, which consists for the most part of linin; and purifies as above.

Properties. Dazzling white silky needles (Schröder). Mostly a white light powder, or pale-yellow friable grains; occasionally obtained in short prisms from an alcoholic or acetic solution. Melts at 110° to 118° (Pagenstecher). In alcoholic solution it tastes intensely and persistently bitter. Heavier than water. Neutral. Free from nitrogen. Acts as a purgative. — Contains 62·92 p. c. C., 4·72 H., and 32·36 O. (Schroder).

Linin is carbonised when strongly *heated*, evolving an irritating odour. — *Nitric acid* forms with it a brown-red solution, and crystals free from oxalic acid. — *Oil of vitriol*, strong *phosphoric acid*, and *arsenic acid* dissolve it with deep violet colour. — Heated to 100° with *chloride of zinc* for some hours, it yields a reddish mass, which colours water a deep cherry-red (Pagenstecher).

Linin dissolves slightly in boiling *water*. It assumes a yellow colour in aqueous *ammonia* and *potash-ley*, and dissolves therein, forming solutions which are precipitated by acids (Buchner). — It dissolves in *chloroform* (Schröder); in strong *acetic acid*, from which it is precipitated by water; in absolute *alcohol* in almost all proportions; sparingly [easily (Schröder)] in *ether*, and to a very slight extent in *volatile oils*. It is taken up from alcoholic solution by *animal charcoal* (Pagenstecher).

47. LIRIODENDRIN. — Occurs to the extent of 2 or 3 per cent. in the fresh root-bark of the tulip-tree, collected in winter. — The powdered bark is digested with alcohol at the temperature of 38°, and the tincture thus obtained is concentrated to ⅕th its volume and allowed to cool, whereupon liriodendrin is deposited in yellow drops, which solidify on cooling. The decanted liquid is evaporated to the consistence of honey, and mixed with ammonia, which precipitates the remainder of the liriodendrin. The collected product is washed with potash-ley so long as it imparts colour thereto, then dissolved in strong alcohol at 38°, mixed with water at the same temperature, and allowed to cool, whereupon crystals are deposited, of which more may be obtained by evaporating the mother-liquor at 38°.

The *hydrated* crystals form colourless rectangular needles or prisms, and also scales resembling boracic acid, having a bitter, not acrid taste. Neutral. Melts at 82°, and sublimes at a somewhat higher temperature with partial decomposition, dense aromatic fumes being evolved at the same time, which condense to a transparent varnish, a brittle brownish resin being left behind. — *Iodine* immediately colours the crystals orange-red; in a cold aqueous solution of liriodendrin it becomes covered with a dull yellow film. — *Chlorine*, passed into alcoholic liriodendrin, forms with it a very bitter resin, which is deposited in transparent granules on evaporating the solution. — *Nitric acid* dissolves it without coloration or evolution of gas; the solution shows no signs of decomposition, even when gently evaporated. — Liriodendrin dissolves in *oil of vitriol*, forming a dark-red solution, from which it is precipitated as a tasteless resin by water. — It is decomposed by hot *hydrochloric acid*, with separation of a green substance.

Liriodendrin is nearly insoluble in cold, but much more freely soluble in boiling *water*. Its solubility is not increased by dilute *acids* or *alkalis*; the latter decompose it when heated. — It dissolves easily in *alcohol* and *ether* (Emmet, *J. Pharm.* 17, 400; *N. Tr.* 24, 2, 274; *Br. Arch.* 39, 44; *Repert.* 75, 88).

48. Loliin. Obtained from the seeds of *Lolium temulentum.* Bley (*Repert.* 48, 169; 62, 175) exhausts the seeds with water; evaporates; exhausts the residue with absolute alcohol; evaporates again; dissolves the residue in water; and, after a third evaporation, dissolves the residue in alcohol. From this solution ether precipitates the loliin as a light dirty-white powder. — Combustible: soluble in cold, more freely in hot water, and in hot alcohol. Has a feebly acid reaction. — Ludwig & Stahl (*N. Br. Arch.* 119, 59, where see their mode of preparation) obtained loliin in the form of a viscid, yellow, bitter-acrid mass, soluble in water, alcohol, and ether-alcohol, and breaking up, under the action of dilute acids, into sugar and volatile acids.

49. Lupinin. — Obtained from lupine-seeds. Deposited from an aqueous solution of the alcoholic extract of the seeds after purification with animal charcoal. Small white, very bitter granules, which turn moist in the air. It is not affected by dilute acids and alkalis, but is decomposed by hot nitric acid, with formation of orange-coloured products. It dissolves easily in weak spirit, but not in absolute alcohol or ether (Cassola, *J. Chim. méd.* 10, 688; *Ann. Pharm.* 13, 308). Landerer (*N. Repert.* 1, 446) obtained in this way crystals soluble in alkalis, and precipitable from the solution by acids.

50. Lycopin. — From *Lycopus europæus.* An aqueous extract of the leaves of the plant is exhausted with alcohol; the alcoholic liquid is freed from most of the leaf-green by precipitation with water and evaporated; and the residue is dissolved in ether and water alternately so long as these liquids leave a residue. — Colourless, transparent amorphous mass, inodorous and very bitter. Softens in water, and runs together in semi-fluid drops when heated therein. Dissolves in 500 pts. of boiling water, forming a solution which becomes cloudy on cooling; not more freely in dilute acids and alkalis, but easily in warm glacial acetic acid, from which solution it is precipitable in white flocks by water. Dissolves very easily in alcohol and ether (Geiger, *Repert.* 15, 11).

51. Marrubiin.

Harms. *N. Br. Arch.* 83, 144; 116, 141.
Kromayer. *N. Br. Arch.* 108, 257; *Chem. Centr.* 1862, 58; *Kopp's Jahresber.* 1861, 747.

The bitter principle of *Marrubium vulgare.* Discovered by Mein.

Preparation. The dried plant is treated three times with hot water; the infusion is evaporated to a syrup which is treated with alcohol; the alcoholic liquid is distilled; and the dark-brown residue is shaken with chloride of sodium and ether, the latter of which takes up the bitter principle and leaves it on spontaneous evaporation. The product is purified by recrystallisation from alcohol, the formation of crystals being facilitated by adding boiling water to the alcoholic solution till turbidity is produced, and then leaving it to cool. 25 pounds of the plant yield 2 grammes of marrubiin (Harms). — Kromayer frees the sap of the plant from albumin, and agitates it with animal charcoal, which takes up the marrubiin. He then boils the charcoal with alcohol; removes tannic acid from the solution by mixing it with water till turbidity is produced, and agitating with hydrate of lead; treats the filtrate with hydrosulphuric acid; filters; evaporates; and purifies the product by dissolving it in ether, or by dissolving it in a large quantity of hot water, mixing the solution with alcohol, and evaporating slowly; by this process, however, most of the marrubiim is obtained in the amorphous state. Crystals are more abundantly obtained by boiling the expressed herb with water, shaking the decoction with animal charcoal, boiling the charcoal with alcohol, evaporating the tincture, treating the residue with ether, and evaporating. — Dissolving it in hot liquids easily renders the marrubiin amorphous, but it crystallises again from the alcoholic solution on standing (Harms).

Properties. Colourless stellate groups of needles (Harms). Obtained from alcohol in needles, and from ether in colourless tables resembling gypsum (Kromayer). Melts at 148° (Harms); at 160° to a colourless oil, which solidifies in a crystalline mass on cooling (Kromayer). Tastes very bitter and somewhat harsh. Neutral. — Becomes slightly coloured in the air.

Marrubiin, submitted to *dry distillation* in a tube, yields oily drops: heated on *platinum foil*, it burns, emitting irritating vapours. — It dissolves in *oil of vitriol* with brownish-yellow colour; is not affected by hot strong *hydrochloric acid;* and dissolves in *nitric acid* only when heated. — Not decomposed by aqueous *alkalis.* — Reduces an ammoniacal solution of silver oxide on boiling (Kromayer).

It is nearly insoluble in *water*, either cold or boiling, but easily soluble in *alcohol* and *ether*. Water throws down oily drops from the alcoholic solution; but on adding water to the solution till turbidity is produced and leaving the mixture at rest, crystals are produced. The solutions are not precipitated by metallic salts or tannic acid, and are not coloured by ferric chloride (Kromayer).

52. **Maticin.** — Obtained from the leaves of the matico plant. An

aqueous decoction of the plant is precipitated with neutral acetate of lead; the filtrate is freed from dissolved lead and evaporated to a syrup, which is dissolved in alcohol; and the solution is again evaporated. Yellowish-brown very bitter extract, soluble in alcohol and in water, but not in ether. It is precipitated from its aqueous solution by potash and ammonia (Hodges, *Phil. Mag.* 25, 202; *Handwörterb.* 5, 141).

53. Mudarin. — From the bark of the root of *Calotropis Mudarii*, which acts as an emetic. It is taken up from the alcoholic extract by water. Pale-brown, amorphous, brittle, inodorous mass, having a nauseous bitter taste. Dissolves easily in cold water; the solution becomes turbid at 23° and is converted at 35° into a jelly, which contracts to a pitchy mass at a higher temperature, and after cooling redissolves only after prolonged contact with water. Dissolves easily in alcohol but not in ether, oil of turpentine, or olive oil (Duncan, *Phil. Mag.* 10, 465; *Berz. Jahresb.* 12, 269).

¶ 54. Murrayin. A glucoside discovered by de Vrij in the flowers of *Murraya exotica*, and examined by Ch. Blas (*Belg. Acad. Bull.* [2], 26, 303; *Jahresb.* 1868, 770). The petals are boiled with water; the extract is evaporated; and the residue is treated with cold water to remove sugar and easily soluble bodies, then with absolute alcohol, which dissolves murrayin together with murrayetin. By precipitating the alcoholic solution with acetate of lead, removing the dissolved lead with sulphuretted hydrogen, evaporating, and recrystallising from absolute alcohol, the murrayin is obtained pure.

White light powder composed of small needles, scentless, but having a slightly bitter taste; exerts no particular action on the animal organism. Melts at about 170°, and yields a crystalline sublimate.

	at 115°.		Blas.		*Air-dried.*			Blas.
36 C	216	51·27	52·11	51·27	$C^{36}H^{22}O^{20}$	398	97·79	
22 H	22	5·53	5·70	6·00	HO	9	2 21	2·7
20 O	160	10 20						
$C^{36}H^{22}O^{20}$	398	100 00			+ aq.	407	100·00	

Heated with dilute *sulphuric acid* (best in sealed tubes) it is resolved into dextroglucose and murrayetin:

$$C^{36}H^{22}O^{20} + 2HO = C^{12}H^{12}O^{12} + C^{24}H^{12}O^{10}.$$

100 pts. murrayin yield 45 pts. glucose; calc. 45·25 pts.

Murrayin dissolves slightly in cold water, with moderate facility in boiling water, and remains as a jelly when the solution is evaporated. In aqueous alkalis and alkaline carbonates, also in alkaline earths, it dissolves easily, the solutions exhibiting a greenish-blue fluorescence, due to the presence of murrayetin. It dissolves abundantly in alcohol, scarcely at all in ether.

Murrayetin prepared as above separates on cooling as a light white crystalline mass made up of small needles. It is tasteless and scentless; melts at 110°, and sublimes partially without decomposition. All its solutions exhibit a strong blue fluorescence, like that of quinine-solutions.

	at 100°.		Blas.			*Air-dried.*		Blas.
24 C	144	61·01	60·86	62·11	$C^{24}H^{12}O^{10}$	236	96·33	
12 H	12	5·09	4·64	5·16	HO	9	3·67	3·6
10 O	80	33·90						
$C^{24}H^{12}O^{10}$	236	100·00			+ aq.	245	100·00	

Dissolves sparingly in cold, freely in boiling *water*, easily also in *alcohol*, less in *ether*. Alkalis and *alkaline earths* dissolve it abundantly, with yellowish colour and strong fluorescence, which, however, disappears on heating the solution, and is not reproduced by addition of acids. *Ferric chloride* colours the aqueous solution bluish-green. Neutral *lead acetate* forms a yellow precipitate soluble in acetic acid and in basic lead acetate. The latter solution precipitates murrayetin immediately; but the precipitate redissolves during washing, with the exception of a small quantity of murrayetin free from lead. An alcoholic solution of murrayetin forms with an alcoholic solution of *hydrate of baryta*, a yellow pulverulent precipitate containing 28·5 p. c. baryta (Blas). ¶

55. NARCITIN. Occurs in the flowers, and more abundantly (to the extent of 37 p. c.) in the bulbs of *Narcissus Pseudonarcissus.* — White, transparent, of faint odour and taste. Causes vomiting. Deliquescent; soluble in water, alcohol, and vinegar (Jourdain, *J. Chim. méd.* 16, 330).

56. NARTHECIN, NARTHECIC ACID, and other constituents of *Narthecium ossifragum. α. Narthecic acid.* The comminuted plant is treated repeatedly with water containing soda, and the extracts are acidified with acetic acid and precipitated, first with neutral acetate of lead, which throws down colouring matter, afterwards with the basic acetate. The latter precipitate is collected, washed, and decomposed with hydrosulphuric acid. The liquid filtered from the sulphide of lead is evaporated to an extract and treated with ether, which takes up narthecic acid. A further quantity may be obtained in white crystals by washing the sulphide of lead with hot water, and slowly evaporating the washings. — White lustrous needles, composed of microscopic, oblique rhombic prisms. Tastes strongly acid. Decomposes when heated, with separation of carbon. Dissolves in water and combines with alkalis and alkaline earths, to form non-crystallisable compounds which are soluble in water. The potash-salt gives with neutral acetate and nitrate of lead, white precipitates, soluble in acids; with ferric chloride a yellowish, with cupric sulphate a whitish-green, with mercuric chloride a white, and with nitrate of silver a white precipitate, the last of which speedily turns red. — The acid dissolves in alcohol and ether.

β. Narthecin. — The plant, previously treated with water, is exhausted with alcohol; the tincture is precipitated with neutral acetate of lead; the filtrate is treated, first with hydrosulphuric acid, then with animal charcoal, and afterwards distilled, to separate most of the alcohol, and left to evaporate spontaneously. The resulting warty deposit is purified by crystallisation from ether. — Friable white mass, melting to a yellow oil at 35°. Tastes very harsh, and has an acid reaction. Not volatile without decomposition. Burns with emission of a repulsive odour. Dissolves in sulphuric acid with brown colour;

in nitric acid with yellow colour, without evolving gas; and is precipitated from these solutions by water. Dissolves slightly in water, and easily in alkalis, from which it is precipitated by acids.

γ. *Resin-acid of Narthecium.* — Extracted from the plant previously treated with water containing soda, and with alcohol, by again treating it with alkaline water (!), and precipitating the golden-yellow solution with acids. Combustible. Decomposed by oil of vitriol and fuming nitric acid. Insoluble in water; soluble in aqueous alkalis with dark-yellow colour, and precipitated therefrom by neutral acetate of lead; soluble also in alcohol, but not in ether.

δ. *Colouring Matter of Narthecium.* — This body is precipitated by basic acetate of lead from the extracts of the plant prepared with alkaline water according to 1, and remains in the extract from which narthecic acid is taken up by ether. On treating this extract with water and aqueous alkalis in succession, a residue is left, from an alcoholic solution of which, water throws down the colouring matter as a yellowish-red powder. — Loose ochre-coloured powder, soluble in oil of vitriol with greenish-brown colour, and decomposed by nitric acid, with evolution of gas. Insoluble in water, aqueous alkalis, and ether, but soluble in alcohol (Walz, *N. Jahrb. Pharm.* 14, 345; *N. Br. Arch.* 105, 257; *Kopp's Jahresber.* 1860, 545).

Concerning the poisonous properties of *Narthecium ossifragum*, see *Botan. Zeitung*, 1866, 351, where Buchenau states, according to a communication from Wöhler, that von Uslar has sought in vain for a peculiar principle in narthecium.

57. NIGELLIN. — Obtained from the seeds of *Nigella sativa*. A tincture of the seeds prepared with 80 p. c. alcohol separates on distillation into an oily and an aqueous layer, the latter of which is agitated with ether so long as it gives up fat. After separating the ether, the liquid is diluted with water, which throws down resin. This is removed; the liquid is precipitated with basic acetate of lead; and the filtrate is treated with hydrosulphuric acid, again filtered from sulphide of lead, and evaporated. The residue thus left is exhausted with alcohol, which leaves nigellin on distillation. — It is a yellow mass of the consistence of turpentine, having an odour of fennel and an intensely bitter taste. Combustible. Treated with nitric acid, it yields oxalic acid and a yellow substance resembling picric acid. The aqueous solution exhibits, on addition of ammonia, lime-water, or baryta-water, a fine green fluorescence, which is destroyed by acids. It precipitates basic acetate of lead, mercurous nitrate, and corrosive sublimate, but no other metallic salts (Reinsch, *Jahrb. pr. Pharm.* 4, 384).

58. PALICOURIN. PALICUREIC ACID. PALICUREA-TANNIC ACID.— Constituents of *Palicourea Marcgravii*, a Brazilian plant of the rubiaceous order. See Pecholt (*N. Br. Arch.* 127, 93).

59. PARATODO BITTER. — Obtained from the bark by exhausting with water that portion of the alcoholic extract which is insoluble in ether, precipitating with neutral acetate of lead, filtering and evaporating, whereupon the bitter is left as a yellowish-brown extract mixed with acetate of potash. Neutral, deliquescent, easily soluble in alcohol.

insoluble in ether. Precipitated by basic acetate of lead, corrosive sublimate, nitrate of silver, and tannic acid (Henry, *J. Pharm.* 9, 410). It is also precipitated by bichloride of platinum; and may be separated from its tannic acid compound in the original state by means of lime (Winckler, *Repert.* 92, 42).

60. PHYCIC ACID. — Contained to the amount of 1 p. c., together with erythroglucin (xii, 385), in *Protococcus vulgaris*, one of the *Algæ*. It is deposited from an alcoholic extract of the plant on concentration, and is purified by washing with ether and recrystallising from hot alcohol. — White opaque needles, of sp. gr. 0·896, without odour or taste, and permanent in the air. Melts at 136° to a brownish liquid, which solidifies in the crystalline state. Neutral. Contains, on the average, 70·22 p. c. C., 3·72 N., 11·76 H., and 14·30 O. — It boils at 250°, undergoing decomposition and yielding an oily distillate. Warm nitric acid decomposes it, producing a light oil and crystals. — Insoluble in water, but soluble in oil of vitriol, from which it is precipitated by water. Forms with the alkalis, crystalline neutral salts, whose solutions froth like soap and are decomposed by carbonic acid. The white insoluble silver-salt blackens on exposure to light. — The acid dissolves in alcohol, in ether, and in oils both fixed and volatile (Lamy, *N. Ann. Chim. Phys.* 35, 129; *Ann. Pharm.* 81, 369).

61. PLUMBAGIN. — Exists in the roots of *Plumbago europæa.* The roots, in not too woody a state, and preferably the more acrid, barky portions, are exhausted with warm ether; the tincture is evaporated; the black residue is boiled with water, which takes up plumbagin and gallic acid, and filtered boiling; the plumbagin, which is deposited on cooling, is collected; the supernatant water is again boiled with the black residue; and this process is repeated so long as plumbagin is deposited on cooling. The product is purified by recrystallisation from ether or ether-alcohol. — Very delicate, fragile, pomegranate or lemon-yellow tufts of needles, which melt at a gentle heat and solidify in radiated crystals on cooling. When it is heated, a portion sublimes unaltered, whilst another portion is decomposed, with deposition of carbon. — It dissolves very slightly in cold, more freely in hot, water, forming lemon-yellow or pomegranate-yellow solutions. With cold oil of vitriol, it forms a pomegranate-yellow solution, which is precipitated by water: larger quantities of sulphuric acid also increase the solvent power of water for plumbagin. Aqueous ammonia and potash dissolve plumbagin freely; and when added in small quantities to the aqueous solution, colour it a cherry-red, which changes to yellow again on addition of acids. — Basic acetate of lead throws down from aqueous plumbagin a carmine-red precipitate, the liquid remaining red. Cupric sulphate colours the solution reddish; very dilute ferric chloride a dirty red. The aqueous solution is not affected by tartar emetic, nitrate of lead, neutral acetate of lead, mercurous nitrate, or tincture of galls. — Plumbagin dissolves easily in cold and hot alcohol, and is thrown down therefrom in thick yellow flocks by water. It is freely soluble in cold and warm ether (*J. Dulong*, 14, 411).

62. QUERCIN. — Contained in oak-bark. To be distinguished from quercite (xv, 215). A decoction of the bark in water containing sul-

phuric acid is precipitated with milk of lime and filtered; the filtrate is precipitated with carbonate of potash and evaporated to an extract, which is exhausted with alcohol; and the alcoholic liquid is evaporated to crystallisation. — Or the bark is boiled with milk of lime; the decoction precipitated with carbonate of potash; and the filtrate decolorised with animal charcoal, evaporated, and left to crystallise. — Small white, very bitter crystals, inodorous and neutral. It assumes an orange-yellow, afterwards brown colour, in oil of vitriol, and is decomposed by hot nitric acid, with separation of yellow flocks. Dissolves in 13·7 parts of water at 19°, and more freely in boiling water, forming a solution which is not precipitated by metallic salts, .gelatin, or tannic acid. Dissolves in hydrochloric and acetic acids, crystallising therefrom on evaporation; and in dilute potash-ley and lime-water, from which it is partially precipitated by more potash or lime. Less freely soluble in spirit than in water; insoluble in absolute alcohol, ether, and oil of turpentine (Gerber, *N. Br. Arch.* 31, 167; *Berz. Jahresber.* 24, 536).

¶ 63. Rhinanthin. A colourless crystallisable glucoside, which occurs in the seed of *Rhinanthus buccalis*, Wallroth, *Alectorolophus hirsutus*, Reichenbach, and is the cause of the violet-colour of bread made with rye-flour contaminated with these seeds. It is neutral, free from nitrogen, has a bitter-sweet taste, dissolves easily in water and in alcohol, is not precipitated by basic acetate of lead. Its alcoholic solution heated with sulphuric or hydrochloric acid, assumes a blue-green colour. .The aqueous solution boiled with sulphuric acid deposits blue-green flocks, while sugar remains dissolved. Nitric acid quickly colours the solution of rhinanthin deep brown (H. Ludwig, *Arch. Pharm.* [2], 136, 64). ¶

64. Samaderin. — Obtained from the bark and fruit of *Samadera indica*, a Java plant of the order *Simarubaceæ*. Obtained from an aqueous extract of the plant by treating it with a small quantity of alcohol, which leaves samaderin undissolved; purified by dissolving it in water and decolorising the solution with animal charcoal. — White feathery laminæ, having a persistent, intensely bitter taste. Neutral. When heated, it melts, evolves bitter acrid fumes, and burns, leaving charcoal. — It is coloured yellow by nitric and hydrochloric acids, and a transient violet-red by oil of vitriol, the solution then depositing feathery crystals. Dissolves in water, forming a solution which is not precipitated by metallic salts, tincture of iodine, or chromate of potash. Less freely soluble in alcohol than in water (*N. Br. Arch.* 96, 265; *Chem. Centr.* 1859, 92).

65. Scrophularin. — Obtained from *Scrophularia nodosa* and *S. aquatica*. When an aqueous decoction of the plant is precipitated with neutral and basic acetate of lead in succession, freed from excess of lead, and then precipitated with tannic acid, this last precipitate contains the bitter principle. The precipitate is treated with alcohol, the alcoholic liquid digested with oxide of lead, filtered, treated with animal charcoal, and evaporated to crystallisation. — Bitter, slowly soluble in water, precipitable in white flocks by tannic acid (Walz, *Jahrb. pr. Pharm.* 26, 296; 27, 12).

66. BITTER OF SENNA-LEAVES. — From these leaves, colouring matters, resin, a bitter principle, and an acid have been obtained; mixtures of these substances have also been described as peculiar bodies.

a. The *colouring matter of Senna-leaves* and husks, distinguished by Feneulle as senna-yellow, and by Bley & Diesel as yellow resin or chrysoretin, is, according to Martius, chrysophanic acid (xvi, 171), which view is supported by Batka. — When the leaves are treated with potash-ley, the filtrate precipitated with hydrochloric acid, and the precipitate washed, dried, and exhausted with chloroform, crystals of chrysophanic acid are obtained on evaporation (Batka, *Chem. Centr.* 1864, 623).

b. Resins of Senna-leaves have been obtained by Heerlein (*Repert.* 79, 219); Buchner (*Repert.* 88, 181); also by Bley & Diesel. They are not purgative.

c. The bitter principle of Senna-leaves is the cathartin of Lassaigne & Feneulle, the sennepicrin of Ludwig. The former is a reddish-yellow, transparent, purgative and deliquescent extract, which is contained in that portion of the aqueous decoction of the leaves which is soluble in alcohol and not precipitable by neutral acetate of lead. According to Peschier & Jacquelin, this cathartin is identical with cytisine (p. 193), and according to Hubert, with rhamno-cathartin (xvi, 72, 81). — Ludwig obtains his sennepicrin from the alcoholic extract of the leaves. The alcohol is distilled off; the residue evaporated with granulated animal charcoal, which takes up the sennepicrin; and the charcoal is washed with cold water and boiled with alcohol. The alcoholic liquid thus obtained is distilled, and the residue is evaporated to dryness with oxide of lead, and again exhausted with alcohol. This extract is freed from lead by hydrosulphuric acid and partially evaporated; the crystals of phosphate of potash then deposited are separated by filtration; and the filtrate is further evaporated. The residue contains *sennacrol* and sennepicrin, the former of which may be separated by agitation with ether, in which the latter is insoluble. Sennepicrin is a brownish-yellow friable substance, resembling jalap-resin and having a sweetish-bitter warm taste. It dissolves in water, forming a solution which is coloured red by alkalis, and green by ferric chloride, and gives a yellowish precipitate with tannic acid. By boiling it with dilute acids, it is resolved into an aromatic volatile oil, and sugar. Sennacrol is decomposed in a similar manner (Ludwig). Binswanger (*Repert.* [3], 4, 64) had previously obtained senna-bitter by precipitation with animal charcoal.

Lassaigne & Feneulle (*Ann. Chim. Phys.* 16, 18; *J. Pharm.* 7, 548). — Bley & Diesel (*N. Br. Arch.* 55, 272). — Winckler (*Jahrb. pr. Pharm.* 19, 263). — Martius (*Pharm. Viertelj.* 6, 604). — Ludwig (*N. Br. Arch.* 119, 50; *Chem. Centr.* 1865, 175).

d. Dragendorff & Kubly (*Russ. Pharm. Zeitschr.* 4, 429 and 465; *N. Repert.* 15, 275; abstr. *Krit. Zeitschr.* 9, 411) distinguish the active principle of senna-leaves as cathartic acid. The same or a similar acid is said to occur in rhubarb and in the bark of the buckthorn. Besides this body, senna-leaves are said to contain chrysophanic acid, sennepicrin, sennacrol, and cathartomannite.

α. Cathartic acid. — $C^{180}N^2H^{96}SO^{82}$. A hot aqueous infusion of the leaves is evaporated to a syrup, mixed with an equal volume of absolute alcohol, which throws down mucus and salts, and filtered. The filtrate is further precipitated with absolute alcohol, and crude cathartic acid is obtained from the precipitate by washing it with absolute alcohol, dissolving in a small quantity of water, adding a few drops of hydrochloric acid to throw down albumin, and precipitating with more hydrochloric acid. Purification is effected by dissolving the product in hot 60 p. c. alcohol and precipitating with ether. — It dissolves in alkalis and is precipitated from the solutions by acids.

The acid contains 57·64 p. c. C., 4·79 to 5·23 H., 1·50 N., and 0·52 to 0·89 S.; the silver salt 33·74 p. c. AgO; the lead-salt 43·23 p. c. PbO. From these numbers Dragendorff & Kubly deduce the formula $C^{180}N^2H^{96}O^{82}S$, the silver-salt containing 8 AgO. in place of 8 HO., and the lead-salt 12 PbO. in place of 8 HO. — It breaks up, on boiling with alcoholic hydrochloric acid, into 34·1 p. c. of sugar, and 65·9 of *cathartogenic acid*, which forms a dirty yellowish-brown powder, containing 62·09 p. c. C., 2·46 H., 4·76 N., and 1·06 S., corresponding with the formula $C^{128}N^2H^{58}O^{46}S$.

The bark of *Rhamnus Frangula* contains a substance similar to cathartic acid, procured in the same manner, and containing 57·52 p. c. C., 5·36 H., 1·04 N., and 0·58 S. By decomposition with alcoholic hydrochloric acid, it yields a product which corresponds to catharthogenic acid, and gives up to ether an aurora-red crystalline substance (Kubly, *N. Repert.* 15, 295).

β. Chrysophanic acid. — On evaporating the alcoholic mother-liquors of cathartic acid to a syrup, agitating with ether, and evaporating the ethereal solution, there is left a yellow oil, which, by treatment with cold alcohol, yields crude chrysophanic acid or a similar body. This substance forms reddish-brown amorphous masses and nodules containing 61·56 p. c. C., and 5·33 H. (See xvi, 171). No chrysophanic acid is obtained by Batka's process.

γ. Cathartomannite. — $C^{42}H^{44}O^{38}$. — The syrupy liquid exhausted with ether to obtain chrysophanic acid (see above) still contains in solution sennepicrin, sennacrol, and cathartomannite. It is exhausted with alcohol; the alcohol is distilled; the residue is dissolved in water and precipitated with neutral and basic acetate of lead; the filtrate is freed from lead and evaporated, and the residue is covered with a layer of absolute alcohol, in which crystals make their appearance after standing for some days. — White, sweet, crystalline nodules, which rotate a ray of polarised light to the right [51·3° (for αj ?)] and do not smell of caramel when heated. It is not susceptible of fermentation, and does not reduce salts of mercury, gold, or platinum, or copper-salts even after boiling with acids. It dissolves easily in water, and prevents the precipitation of copper oxide by alkalis. Slightly soluble in spirit, but not in ether or absolute alcohol. Contains 41·68 p. c. C., 7·42 H., and 50·90 O.

ε. According to Rau (*Pharm. Viertelj.* 16, 92) the alcoholic tincture of senna-leaves does not contain any purgative substance. The leaves, previously exhausted with alcohol, do not give up chrysophanic acid to benzol; neither is this body obtained by the dry distillation of the leaves. The active principle of the leaves, according to Rau, is precipitable by basic acetate of lead; he believes, however, that he has obtained it in crystals, by the following process, from that portion of the decoction of the leaves which is not precipitated by the basic acetate. The decoction is precipitated with basic acetate of lead, which throws down leaf-green, chrysoretin, resin, and gum; the filtrate is treated with hydrosulphuric acid: and the precipitated sulphide of lead is exhausted with ether. The ethereal solution deposits, by spontaneous evaporation, white needles, having a nauseous bitter taste; fusible, combustible, neutral, insoluble in water, acetic acid, alkalis, and cold alcohol, but soluble in hot alcohol, ether, and chloroform. These needles are the active principle (Rau).

67. SPIGELIA BITTER. — Brown extract, contained in that portion of the aqueous extract of *Spigelia anthelmia* which is soluble in alcohol and not precipitable by neutral acetate of lead. According to Feneulle, it acts as a narcotic, but according to Ricord Madiana (*Br. Arch.* 25, 38) it does not possess this property. It is soluble in water and alcohol, insoluble in ether (Feneulle, *J. Pharm.* 9, 197).

68. SPILANTHIN. — Occurs in *Spilanthes oleracea* (*Handbuch.* viii, 68) at the time of flowering. It is taken up by ether from an alcoholic extract of the plant, and is obtained in crystals by evaporating the ethereal solution, dissolving the residue in a small quantity of absolute alcohol, adding water till turbidity is produced, and setting the solution aside. — White light needles, which run into a resinous mass when their solution in ether or alcohol is rapidly evaporated. Not precipitable by neutral acetate of lead (Walz, *N. Jahrb. Pharm.* 11, 283). Besides this body, the plant contains an acrid substance. See Buchner (*Repert.* 38, 366); Lassaigne (*J. Chim. méd.* 1, 261).

69. TANACETIN. — Obtained from *Summitates Tanaceti.* Prepared, according to Homolle, in the same manner as digitalin (xvi, 333). — Yellowish-white nodules and granules, inodorous, very bitter, and slightly acrid. When heated, it melts, turns brown, evolves an odour of melilot, and leaves charcoal. — Dissolves in cold oil of vitriol, forming a hyacinth-red solution. It is very slightly soluble in water, but imparts to the liquid its bitter taste. Soluble in ether and less freely so in alcohol (Leroy, *J. Chim. méd.* 21, 357).

70. TANGININ and TANGIN-CAMPHOR. — From the fruit of *Tanginia madagascariensis.* When the fruit is freed from oil by expression, and afterwards exhausted with ether, that liquid takes up tangin-camphor. The residue gives up to alcohol the tanginin, together with an acid body not precipitable by lead-salts. — Tanginin is a reddish-brown, sticky, bitter extract, which reddens litmus and acts as a narcotic. It does not yield ammonia by dry distillation. The aqueous solution is precipitated white by chlorine, bluish-green by acids, reddish-brown by alkalis, and is coloured brown by ammonia; it is likewise precipitated by metallic salts. Tanginin is soluble in alcohol, insoluble in ether.

Tangin-camphor. — Shining, transparent laminæ, which deliquesce in the air and melt at a moderate heat, without volatilising. Neutral, very bitter and burning, poisonous; fatal to animals in small doses.

Free from nitrogen. Insoluble in water, and does not combine with acids. Soluble in alcohol, from which it is precipitated by water; insoluble in ether (O. Henry, *J. Pharm.* 10, 52).

71. Taraxacin. — Obtained from the fresh milky juice of the root of *Taraxacum officinale.* Polex heats the fresh juice to boiling, filters, and concentrates the filtrate, whereupon the taraxacin crystallises. It is purified by recrystallisation from water or alcohol. White, easily fusible crystalline nodules, which have a bitter, somewhat acrid taste, burn when heated, without evolving ammonia, and dissolve in strong acids without coloration. It dissolves with difficulty in cold water, but easily in boiling water, alcohol, and ether (Polex, *N. Br. Arch.* 19, 50). — Kromayer exhausted the coagulated juice with hot water, agitated the aqueous liquid with animal charcoal, which took up the bitter principle, and exhausted the charcoal with alcohol. On distilling off the alcohol, precipitating the residual solution with basic acetate of lead, removing lead by means of hydrosulphuric acid, and evaporating, the taraxacin remained as a colourless amorphous bitter mass (Kromayer, *Die Bitterstoffe*, 97).

The albumin, coagulated by boiling the milk-sap, gives up to alcohol, white cauliflower-like fusible nodules, which have an acrid taste and burn with difficulty. They are but little affected by nitric acid, dissolve in oil of vitriol with yellow colour, carbonise when the solution is heated, and are not precipitated from their alcoholic solution by basic acetate of lead. Easily soluble in alcohol and ether (Polex). These nodules appear to be identical with Kromayer's tasteless *taraxacerin*, which contains 74·44 p. c. C., 12·69 H., and 12·87 O., corresponding to the formula $C^{40}H^{40}O^5$ (Kromayer).

72. Teucrium Bitter. — *From Teucrum Scordium.* — An aqueous solution of the alcoholic extract of the plant is freed from substances precipitable by neutral acetate of lead, and from excess of lead, and evaporated; the bitter is extracted from the residue by ether. — Honey-yellow mass, triturable to a white powder after drying. Neutral. — Insoluble in cold water and dilute sulphuric acid; slowly soluble in aqueous ammonia and potash with golden-yellow colour; soluble in alcohol and ether (Winckler, *Repert.* 38, 252).

73. Vellarin. — From *Hydrocotyle Asiatica.* Bitter, strongly smelling oil, which thickens on exposure to the air, dissolves in ammonia, ether, and weak spirit, but not in potash-ley (Lepine, *N. J. Pharm.* 28, 47; *Chem. Centr.* 1855, 542; *Kopp's Jahresber.* 1855, 723).

74. Bitter principle of the berries of Viburnum Lantana. — The crushed berries are boiled with milk of lime; the filtrate is neutralised with hydrochloric acid and concentrated, then agitated with animal charcoal, which takes up the bitter principle and yields it again to alcohol after washing and drying; and the alcoholic liquid is evaporated to a syrup, and freed from an acrid substance by agitation with ether. Yellow hygroscopic extract, which dissolves in water, tastes very bitter, and cannot be made to crystallise by dialysis (Enz, *Pharm. Viertelj.* 12, 534).

75. Viburnin. — Obtained from the bark of the guelder rose

(*Viburnum Opulus*). It is extracted by boiling water from the ethereal extract of the bark. The aqueous liquid is freed from tannic acid by digesting it with parchment, decolorised by animal charcoal, and evaporated.—Amorphous yellow friable mass, having a pure bitter taste and neutral reaction. Combustible. Dissolves with difficulty in water, easily in alcohol (Kramer, *N. Br. Arch.* 40, 266).

76. VINCIN.—From *Vinca minor*.—An alcoholic tincture of the leaves is concentrated by evaporation, after addition of tartaric acid; the leaf-green thereby thrown down is removed; and the filtrate is supersaturated with bicarbonate of soda and shaken with ether. The ethereal liquid, when evaporated, leaves a brown varnish, which is exhausted with dilute sulphuric acid. A solution is thus obtained from which, after filtration, ammonia throws down a reddish-white precipitate of vincin.—Grey-white powder, soluble with difficulty in water and in dilute hydrochloric and sulphuric acids, forming bitter solutions, which leave an amorphous varnish when evaporated. They are precipitated by carbonate and oxalate of potash, and by tartar-emetic, terchloride of gold, bichloride of platinum, and tannic acid. Vincin dissolves easilyin ether and alcohol, and does not crystallise on evaporating the solutions (Lucas, *N. Br. Arch.* 97, 149).

77. BITTER PRINCIPLE OF WHITE CINNAMON.—The aqueous decoction is freed from resin by cooling, from sugar by crystallisation, and evaporated. The residue is dissolved in absolute alcohol; the solution is evaporated, and the residue is dissolved in ether, which on evaporation leaves the bitter as an amorphous brown soft mass. Softens and dissolves to a slight extent in water (Petroz & Robinet, *J. Pharm.* 8, 197).

COMPOUNDS CONTAINING 68 ATOMS OF CARBON.

Primary Nucleus $C^{68}H^{58}$; *Oxygen-nucleus* $C^{68}H^{56}O^2$.

Leucopetrin.

$$? \; C^{68}H^{56}O^4 = C^{68}H^{56}O^2,O^2.$$

Assuming the correctness of the above formula, Brückner's leucopetrin from peat belongs to this place. See xvii, 441.

Primary Nucleus $C^{68}H^{70}$; *Oxyazo-nucleus* $C^{68}N^2H^{58}O^{10}$.

Samanderine.

$$C^{68}N^2H^{60}O^{10} = C^{68}N^2H^{58}O^{10},H^2.$$

ZALESKY. *Tübinger medic. Untersuch.* 1, 85; abstr. *Krit. Zeitschr.* 10, 62; *Kopp's Jahresber.* 1866, 754.

The poison contained in the secretion of the cutaneous glands of the salamander. — On older investigations of the poison of toads and salamanders. See *loc. cit.*

The secretion obtained by scraping the sides of the head and the back of the animal with a teaspoon, is white, viscid, and strongly alkaline. When mixed with water and heated to 59°, it deposits white curdy flocks, after removing which, a clear, alkaline, and highly poisonous filtrate is obtained. This is precipitated with phosphomolybdic acid; the resulting white curdy flocks are washed and dissolved in baryta-water; excess of baryta is removed by means of carbonic acid, and the filtrate is concentrated, finally in a retort through which a stream of hydrogen is passed. In this process long needles (of the hydrated base, according to Zalesky) are formed, and afterwards disappear, and ultimately there remains a colourless, brittle, amorphous mass. It contains, besides the poisonous, strongly alkaline samanderine, a resin produced by alteration of that body, which combines with hydrochloric acid, is insoluble in water, but dissolves in alcohol, forming a solution which exhibits a transient greenish fluorescence.

	Dried.			Zalesky.	
68 C	408	70·83	70·3	70·9	70·7
2 N	28	4·86	4·8	4·8	
60 H	60	10·42	10·4	10·2	10·4
10 O	80	13·89	14·5	14·1	
$C^{68}N^2H^{60}O^{10}$	576	100·00	100·0	100·0	

Samanderine is not volatile without decomposition. It retains its poisonous properties for months after drying. Its aqueous solution and an aqueous extract of the secretion of the cutaneous glands likewise retain their activity after prolonged boiling, but probably lose it by gradual drying in the air.

Samanderine dissolves in *water*, forming a strongly alkaline solution. On mixing a strong aqueous solution with hydrochloric acid, it yields slender non-poisonous needles, containing 10·6 p. c. of hydrochloric acid ($C^{68}N^2H^{60}O^{10},2HCl$ requires 11·24 p. c. HCl). Its solution is precipitated by *phosphomolybdic acid* and *bichloride of platinum*, and when evaporated with bichloride of platinum, leaves an amorphous transparent blue mass, insoluble in water. — Samanderine dissolves readily in *alcohol.*

Geomyricin.

$$C^{68}H^{68}O^4 = C^{68}H^{68}O^2,O^2.$$

Assuming the correctness of the above formula, Brückner's geomyricin (xvii, 441) from peat belongs to this place.

COMPOUNDS CONTAINING 78 ATOMS OF CARBON.

Excretin.

$$C^{78}H^{78}SO^2 ?$$

W. Marcet. *Proceedings Roy. Soc.* 7, 153; *Phil. Mag.* [4] 9, 65; *Chem. Gaz.* 1854, 378; *J. pr. Chem.* 63, 382; *Instit.* 1855, 119;

Kopp's Jahresber. 1854, 713. — *Phil. Mag.* [4] 14, 310; *Chem. Gaz.* 1857, 277; *Instit.* 1858, 81; *Kopp's Jahresber.* 1857, 565. — *N. Ann. Chim. Phys.* 59, 91; *N. J. Pharm.* 38, 128; *Chem. Centr.* 1860, 586; *Kopp's Jahresber.* 1860, 586.

Occurs in the fæces of man, but not in those of other animals.

Fresh fæces are exhausted with boiling alcohol; the liquid is filtered and allowed to stand; the deposit of margarates and phosphates which is then thrown down, is separated by filtration; the filtrate is mixed with a small quantity of milk of lime, and then with its own volume of water, and left to stand for some hours; and the resulting deposit is washed and dried. This deposit, when treated three or four times with alcohol containing ether, gives up thereto the excretin, which crystallises from the solution on standing and spontaneous evaporation. It is purified by recrystallisation from boiling alcohol, with the help of animal charcoal (the charcoal, which contains some excretin, being ultimately washed with ether) and dried in a vacuum.

Properties. Very light, thin, microscopic, four-sided prisms, with pointed ends. Neutral. Melts at 92° to 96°, and solidifies in a resinous mass on cooling.

Calculation, according to Marcet.			Marcet.
78 C	468	80·97	80·43
78 H	78	13·49	13·52
S	16	2·77	2·78
2 O	16	2·77	3·27
$C^{78}H^{78}SO^2$	578	100·00	100·00

Excretin *heated* on platinum foil melts, emits an aromatic odour, and burns. It evolves red fumes with boiling *nitric acid.* — Not affected by boiling potash-ley.

It is insoluble in cold *water*, and melts to a yellow resin in boiling water. Insoluble in dilute *acids.* — Dissolves with difficulty in cold *alcohol*, but easily in boiling alcohol and in *ether.*

COMPOUNDS CONTAINING 80 ATOMS OF CARBON.

Primary Nucleus $C^{80}H^{70}$.

Fichtelite.

$C^{80}H^{70}$.

C. Bromeis. *Ann. Pharm.* 37, 304; *Berz. Jahresber.* 22, 214.

T. E. Clark. *Ann. Pharm.* 103, 236; *Sill. Amer. J.* 75, 164; abstr. *J. pr. Chem.* 73, 247; *Kopp's Jahresber.* 1857, 701.

Discovered by Fikentscher. Frequently confounded with retene (xvii, 8). — Occurs in fossil pine-trunks from the peat-beds of Redwitz in the Fichtelgebirge, partly separated in the form of colourless flat needles, and partly disseminated through the wood. — Also in cracks in the wood from the Franzensbader peat-beds (Reuss, *Kenng. Jahresber.* 1853, 132).

Preparation. 1. A solution in ether or alcohol of the fichtelite scraped from the trunks, readily yields crystals. — 2. When the comminuted wood is exhausted by prolonged boiling with ether, the ether is distilled off, and the residue mixed with alcohol, a solution is obtained which yields no crystals, even after cooling. It is therefore precipitated with neutral acetate of lead, filtered, freed from lead by means of hydrosulphuric acid, boiled with the sulphide of lead, and filtered after cooling, whereupon the fichtelite crystallises, more especially on placing in the solution a ready-formed crystal (Clark).

Properties. Oblique, prismatic, hemimorphic, generally tabular crystals, having no cleavage-plane (Clark). See his description (*Ann. Pharm* 119, 226). Less lustrous than retene, brittle and hard (Fritzsche). Melts at 46°, and afterwards solidifies only at 36° (Clark); solidifies to a crystalline mass only after long standing (Bromeis). At a temperature above 320° it distils undecomposed. It is lighter than water, heavier than alcohol (Bromeis; Clark).

			Bromeis.	Clark. *mean.*
80 C	480	87·27	88·07	87·13
70 H	70	12·73	10·70	12·86
$C^{80}H^{70}$	550	100·00	98·77	99·99

Bromeis analysed picked crystals of fichtelite: his formula is C^4H^3.

Decompositions. 1. When fichtelite is submitted to dry distillation, a small portion is decomposed, with deposition of carbon. — 2. *Burns* with luminous flame. — 3. It is carbonised by *anhydrous sulphuric acid*, with evolution of sulphurous acid. — *Fuming sulphuric acid* forms a deep-red solution, which slowly evolves sulphurous acid: no conjugated acid is produced. — 4. It is violently attacked by warm fuming *nitric acid*, with evolution of nitric oxide: on concentrating the solution to one-fourth, precipitating with water, and dissolving the precipitate in ether-alcohol, a red oil is obtained, whilst oxalic acid remains in solution. — 5. Fichtelite melted in a current of *chlorine* evolves hydrochloric acid, and forms the chlorinated products $C^{80}H^{68}Cl^2$ and $C^{80}H^{66}Cl^4$ (Clark).

On passing chlorine over a few grammes of fichtelite for half an hour, dissolving the product in ether-alcohol, and separating a little unchanged fichtelite by crystallisation, the solution deposits in succession a colourless oil (*a*) and a yellowish oil. The latter (*b*) is obtained in greater abundance by continuing the current of chlorine for two hours, but it is then mixed with a dark-red oil (Clark).

			Clark. *a.*
80 C	480	77·56	77·21
68 H	68	10·99	11·17
2 Cl	71	11·45	11·30
$C^{80}H^{68}Cl^2$	619	100·00	99·68

			Clark. *b.*
80 C	480	69·79	69·43
66 H	66	9·59	9·73
4 Cl	142	20·62	20·25
$C^{80}H^{66}Cl^4$	688	100·00	99·41

Bromine, acting on melted fichtelite, produces hydrobromic acid and oily bodies similar to the chlorine-compounds, one pale-red (*a*) and another dark-red and viscid (*b*).

			Clark. *a.*
80 C	480	76·31	76·18
69 H	69	10·97	11·03
Br	80	12·72	
$C^{80}H^{69}Br$	629	100·00	

			Clark. *b.*
80 C	480	67·80	
68 H	68	9·61	
2 Br	160	22·59	22·67
$C^{80}H^{68}Br^2$	708	100·00	

Fichtelite dissolves very sparingly in *absolute alcohol*, and very freely in *ether* (Bromeis). — It does not combine with *picric acid* (Fritzsche).

Appendix to Fichtelite.

Earth-resins, some of which appear to be identical with Fichtelite.

1. **Tekoretin.** — Occurs separated in crystals, together with retene (xvii, 8), on fossil fir-trunks in Danish peat-bogs, and crystallises before the retene from a solution of the two in boiling alcohol. — Large colourless crystals, melting at 45° and distilling undecomposed at the boiling point of mercury. Sp. gr. 1·008 at 11°: the melted substance floats on water.

Tekoretin is not affected by potassium. — With *nitric acid* it forms a brown nitrogenous resin and oxalic acid. — When finely divided and treated repeatedly with *chlorine*, it yields an oily body and a yellowish-brown chlorine-compound, $C^{40}H^{22}Cl^8 + HO$, which crystallises on mixing its ethereal solution with boiling alcohol.

Tekoretin dissolves easily in *ether*; in 400 parts of *alcohol* at 5°, and more freely in boiling alcohol (Steenstrup & Forchhammer, *Ann. Pharm.* 41, 42).

			Steenstrup. *mean.*
80 C	480	87·27	87·17
70 H	70	2·73	12·84
$C^{80}H^{70}$	550	100·00	100·01

According to Steenstrup C^5H^4.

2. Scheererite.

STROMEYER. *Kastn. Arch.* 10, 113.
MACAIRE PRINSEP. *Schw.* 55, 320; *Pogg.* 15, 294.
KÖNLEIN. *Bibl. univ.* 36, 316; *Pogg.* 12, 336.
HAIDINGER. *Pogg.* 54, 263.
FRITSCHE. *J. pr. Chem.* 82, 324.

Braunkohlencampher (Gmelin). *Natürliches Naphthalin* (Scheerer). *Prismatisches Naphthalinharz* (Könlein).

Occurs, together with retene (xvii, 8), in a lignite bed at Uznach, St. Gall. — White, somewhat nacreous, translucent, loosely aggregated granules and laminæ, not fatty to the touch, very friable, and slightly heavier than water (Stromeyer). According to Könlein, irregular pyramids, cleavable parallel to the horizontal and vertical angles; having a conchoidal fracture; white, transparent, and brittle; heavier than water. According to Haidinger, six-sided prisms, the angles of which do not differ much from 120°, with the alternate lateral faces obliquely inclined to the P-face. Small lamellar crystals, monoclinic, tabular by predominance of the longitudinal face; a prism likewise occurs. Prism and longitudinal faces vertically striated. Also a clinorhombic hemipyramid and a clinorhombic transverse hemidome, oppositely placed (Fig. 96 with the *m* faces of fig. 97 very fully developed). $u : h = 123° 30'$; $u : c = 101° 30'$; $i : h = 135°$ (Kenngott, *Wien. Acad. Ber.* 14, 272).

Melts at 45° [46° (Haidinger); 44° (M. Prinsep)] to a colourless oil, which solidifies to a mass of needles on cooling, often only after several days in contact with a platinum or glass rod (Stromeyer). Sp. gr. 1·05 to 1·2 (Breithampt); a little heavier than water (Konlein; Stromeyer); lighter than water (sp. gr. 0·65 !) (M. Prinsep). Boils above 100°; volatilises entirely without decomposition and sublimes in needles (Stromeyer). — According to Prinsep, it volatilises at 92°, at which temperature fichtelite likewise begins to sublime (Fritsche).

According to Prinsep, it contains 73 p. c. C., and 24 H., but Prinsep himself considers the analysis very doubtful, and it cannot therefore be regarded as a proof of the difference of fichtelite and scheererite. See Clark and Fritsche, who consider the two bodies as very probably identical. Kenngott's description of the easily fusible crystals from Uznach, however, does not agree with that of fichtelite given by Clark.

Scheererite *burns* with a slightly smoky flame, emitting an odour of pitch (Haidinger). — In *chlorine* it melts in a few minutes, and afterwards solidifies to a granular crystalline mass, which is not further acted upon by chlorine. — It is very slowly decomposed by strong nitric acid. — Dissolves in *oil of vitriol*, and on prolonged digestion therewith forms a conjugated acid (Stromeyer) (Was retene likewise present? Kr.). Scheererite dissolves easily in *alcohol*, from which it crystallises; also in *acetate of ethyl*, *ether*, and *volatile* and *fixed oils*.

3. Branchite. Savite.—From Monte Vaso in Tuscany. Colourless transparent mass, which melts at 75°, turning yellow and solidifying in the amorphous state on cooling. Burns without residue. Crystallises from alcohol in fine laminæ. Sp. gr. 1·00 (Savi, *Kenngott's Jahresber.*

1844—1849, 254); 1·0442 (Piria). After crystallisation from alcohol it contains 87·0 p. c. C., 13·4 H., corresponding to the formula C^9H^8 (Piria, *Kopp's Jahresber.* 1855, 984).

Lignite from the Wilhelmszech mine in the Westerwald contains a resin melting at 75° and otherwise agreeing with scheererite, probably branchite (Casselmann, *Ann. Pharm.* 89, 50).

4. **Hartite.** — Occurs in lignite from Oberhart, near Gloggnitz in Lower Austria (Haidinger, *Pogg.* 54, 261). Also in a lignite-bed at Rosenthal in Styria (Kenngott). Spermaceti-like mass and tabular crystals (Haidinger). Brittle and very friable. Sp. gr. 1·046 (Haidinger), 1·041 (Baumert), 1·036 to 1·060 (Kenngott). Melts at 74° (Haidinger), 72° (Baumert). Begins to volatilise at 100°, the vapours condensing to an oil, which solidifies to a crystalline mass. According to Kenngott, it distils easily, for the most part unaltered. According to Schrötter, it distils in the form of a yellow oil, at a high temperature only. According to Kenngott, it distils also with aqueous vapour. It is not attacked by cold oil of vitriol; the mass blackens only above 100°. with evolution of sulphurous acid. It is not acted on by melted potassium. — Dissolves slightly in alcohol and very freely in ether, crystallising from the solution (Schrötter, *Pogg.* 59, 43). According to Baumert, it contains an oxygenated body which may be separated by crystallisation from alcohol. The crystals obtained from ether or alcohol are thin rhomboïdal laminæ with angles of 99½° and 80½°, frequently having the more acute angles truncated, so that the truncation-face forms with the longer side of the rhomboïd an angle of 117½°, and with the shorter side an angle of 143° (Kenngott, *Jahresber.* 1856 and 1857, 186).

			Schrötter. *mean.*	Baumert.
6 C	36	87·80	87·49	87·77
5 H	5	12·20	12·08	12·26
C^6H^5	41	100·00	99·57	100·03

Schrötter's hartite was purified by fusion and decantation; Baumert's by recrystallisation.

5. Hatschetin.

CONYBEARE. *Phil. Ann.* 1, 136.
JOHNSTON. *Phil. Mag.* 12, 338; abstr. *J. pr. Chem.* 13 to 38.

A fossil resin occurring in ironstone in South Wales (Conybeare); in Glamorganshire (Johnston). Hatschetin occurring in sphærosiderite at Rossitz in Moravia resembles ozokerite, but is softer, melts at 71°, has the sp. gr. 0·892, dissolves easily in oil of turpentine, with difficulty in ether, and is insoluble in alcohol (Rittler, *Kopp's Jahresber.* 1849, 781; Fötterle, *Kenngott's Jahresber.* 1854, 140).

Hatschetin possesses a scaly or granular texture, is somewhat softer than tallow, yellowish-white or yellow, translucent, slightly nacreous or dull (Conybeare). Transparent yellowish thin laminæ, having a pearly lustre. Sp. gr. 0·916 at 15° (Johnston). Melts below 77° (Conybeare); at 46° (Johnston). Inodorous in the cold, but has a fatty odour when heated.

When carefully *heated*, it appears to distil unchanged (Johnston), yielding a greenish-yellow buttery distillate, of bituminous odour, and leaving charcoal (Conybeare). *Burns* with flame from a wick (Conybeare). — Turns dark and opaque in the *air*. — Carbonises in boiling *oil of vitriol*, but is not decomposed by boiling *nitric acid* (Johnston).

Hatschetin dissolves very sparingly in boiling *alcohol*, and is deposited almost entirely on cooling. Its solution in warm ether first deposits delicate laminæ and then solidifies to a mass resembling opodeldoc (Conybeare).

It contains 84·73 p. c. C., and 14·62 H. (Johnston).

¶ COMPOUNDS CONTAINING 96 ATOMS OF CARBON.

Theveresin.

$C^{96}H^{70}O^{34}$.

Cl. Blas. *Bull. de l'Académie royale de Médecine de Belgique* [3], 2, No. 9; *N. Jahrb. Pharm.* 31, 1; *Jahresb.* 1868, 768.

Formation and Preparation. By absorbing thevetin (*infra*) with dilute hydrochloric or sulphuric acid, the theveresin then separating as a resinous precipitate, while sugar remains in solution:

$$\underset{\text{Thevetin.}}{C^{108}H^{84}O^{48}} = \underset{\text{Theveresin.}}{C^{96}H^{70}O^{34}} + \underset{\text{Glucose.}}{C^{12}H^{12}O^{12}} + 2HO.$$

100 pts. thevetin yield from 15 to 16 p. c. theveresin, a result agreeing with the equation just given.

The decomposition of the thevetin is most readily effected by heating with dilute sulphuric acid in sealed tubes. The resinous precipitate is purified by repeated solution in alcohol and precipitation with water.

White, easily cohering powder, consisting of $C^{96}H^{70}O^{34} + HO$, and giving off 4 at. water (3·2 p. c.) at 110°. Melts at 140°, and decomposes at a higher temperature without yielding a sublimate. With strong *sulphuric acid* it behaves like thevetin. — Dissolves sparingly in cold, somewhat more easily in boiling *water*, is moderately soluble in *alcohol*, very slightly in *ether*, insoluble in *chloroform* and in *benzol*. The solutions have a bitter taste, and neutral reaction. In *alkalis* it dissolves with yellow colour. The alcoholic solution is not precipitated by metallic salts.

Conjugated Compounds of Theveresin.

Thevetin.

$$C^{108}H^{84}O^{48} = C^{96}H^{70}O^{34},C^{12}H^{12}O^{12},2HO.$$

Blas. *Loc. cit.*

A glucoside occurring in the seeds of *Thevetia nereïfolia*, Juss., or *Cerbera thevetia*, Lin., and perhaps identical with the substance called *cerberin*, which Oudemans obtained (together with olein and palmitin) from the seeds of *Cerbera Odollam*, an East Indian plant (*Jahresb.* 1866, 697).

The mass remaining after the oleaginous seeds have been pressed, is first treated with ether till the fats are completely removed, then with cold water, and finally boiled with alcohol. The alcoholic extract on cooling, deposits thevetin, which may be purified by repeated crystallisation.

White powder consisting of small crystalline laminæ, inodorous and having a very bitter taste. When dried over oil of vitriol it contains $C^{108}H^{84}O^{48} + 6HO$. It gives off 2 at. water at 110°, melts at about 170°, and decomposes at a higher temperature. Dissolves in 122 pts. *water* at 14°, more abundantly in hot water, easily also in *alcohol*, but is insoluble in *ether*. *Glacial acetic acid* dissolves it abundantly, and the solution turns the plane of polarisation to the left. According to de Vrij (who first prepared this substance), the molecular rotatory power is $\alpha = -85{\cdot}5°$. Solutions of thevetin are not precipitated by any metallic salt. Strong *sulphuric acid* dissolves it with red-brown colour, soon changing to cherry-red, and after a few hours to violet; on addition of water the colour disappears. Its decomposition by boiling with dilute acids has been already mentioned. ¶

End of Compounds arranged according to the number of the Carbon-atoms.

APPENDIX TO THESE COMPOUNDS.

Animal Proteides, Gelatinous substances, Horny textures, Animal Colouring-matters, Vegetable Proteides, and allied compounds.

1. *Generalities respecting Proteides and allied bodies.*

The name protein, introduced by Mulder (*Berzel. Jahresber.* 19, 639), and employed by him to designate the hypothetical organic radical common to fibrin, albumin, casein, and crystallin, has remained in use even after the refutation of Mulder's protein theory, and serves as a synonym for the expressions *blood-former*, *albuminous substance* (*Handworterb.* 2 Aufl. 2, 2, 120), and likewise as a general term for albumin, casein, and fibrin, and the corresponding vegetable substances. Heintz (*Zoochemie*, 600) includes amongst proteides also horn-substance, fibroin, and the substance of sponge, but excludes glutin and chondrin. — Gerhardt (*Traité* 4, 430) regards the proteides as characterised by the presence of sulphur in their composition.

Hoppe-Seyler (*Handb.* 182) enumerates eleven proteides, viz., serum-albumin, egg-albumin, casein, paralbumin, syntonin, myosin, fibrinogen, fibrinoplasmin, fibrin, coagulated albumin, and amyloïd substance, to which should be added the corresponding vegetable substances. The term proteides is here used in the comprehensive sense, which permits the grouping together of the non-crystallisable nitrogenous animal and vegetable substances possessing reactions in common.

The older researches of Beccaria, Fourcroy, Einhof, Proust, and Vogel, having established the facts of the existence of albuminous substances in the vegetable kingdom, of their similarity to corresponding substances of animal origin, and of the similarity of these last to one another, Mulder (*Berzel. Jahresber.* 18, 534), in 1837, arrived at the conclusion that fibrin, serum-albumin, egg-albumin, silk, and the nitrogenous vegetable bodies which we now call proteides, contained one and the same organic oxide, $2(C^3NH^6),O^5$. This body was said to be combined with sulphur and phosphorus in fibrin, albumin, and vegetable albumin, in the proportion of 50 atoms of the oxide to 1 atom of sulphide of phosphorus, PS^2. On dissolving fibrin or albumin in excess of potash-ley, sulphide of potassium and phosphate of potash were stated to be formed; the precipitate thrown down from the solution by acids was regarded as the oxide free from sulphur and phosphorus, and said to be identically the same whether obtained from fibrin or from albumin. Hence it was regarded as probable that fibrin and egg-albumin contained 1 atom of PS^2, whilst serum-albumin contained 1 atom of PS^4 in combination with 50 atoms of the oxide.

In the following year, Mulder (*Berzel. Jahresber.* 19, 639) extended these views, and modified them in some points. The non-sulphuretted organic oxide, $C^{40}N^5H^{31}O^{12}$, now distinguished as *protein*, in combination with sulphur, phosphorus, and phosphate of lime, was said to form fibrin, albumin, casein, crystallin, &c., serum-albumin and fibrin containing 20 atoms of protein to 1 atom of PS^2, whilst coagulated egg-albumin contained twice as much sulphur. The precipitates thrown down by sulphuric, hydrochloric, and gallotannic acids, from solutions of protein in alkalis (albuminates of the alkalis) or acetic acid, were there described by Mulder as compounds of protein (free from sulphur and phosphorus) with these acids.

After Mulder, in the years 1840—1842, had described numerous other compounds of his hypothetical protein as chlorite of protein, proteinsulphuric acid, trioxyprotein, bioxyprotein, &c., and made known his views with regard to the occurrence and use of these bodies in the organism (*Ann. Pharm.* 47, 300), Liebig showed (*Ann. Pharm.* 47, 300) that the precipitate thrown down by carbonate of ammonia from solutions of fibrin in dilute hydrochloric acid, and described by Mulder as protein-binoxide, really contained sulphur; further, that the precipitate produced by acetic acid in a solution in potash-ley of vegetable casein from beans is not protein free from sulphur, as Mulder supposed, but likewise contains sulphur; and, lastly, that, according to Laskowski's experiments, alkaline solutions of casein, albumin, and fibrin, even after boiling for hours, give with acetic acid, precipitates in which the presence of sulphur may be demonstrated by fusing them with hydrate of potash.

Soon after this, Laskowski (*Ann. Pharm.* 58, 129) further controverted Mulder's protein theory by showing that the formulæ given by Mulder for the albuminous bodies were not in accordance with Mulder's own analyses; that the body prepared by Mulder as protein contained sulphur; and that protein free from sulphur cannot be isolated. Laskowski, indeed, succeeded in obtaining products free, or nearly free, from sulphur, by the prolonged treatment of albuminous bodies with hot potash-ley, but only as the result of far-advanced decomposition.

In his reply Mulder (*Berzel. Jahresber.* 27, 512) declared that the sulphur of proteides, when treated with dilute potash, forms therewith pentasulphide of potassium and hyposulphite of potash, so that, on the addition of acetic acid to the alkaline solution, free sulphur is thrown down with the protein. This admixture of sulphur with the precipitate was said to be prevented by exposing the alkaline solution to the air to oxidise the sulphur-compounds; but on its being shown by Fleitmann (*Ann. Pharm.* 61, 121) that protein thus prepared still contained sulphur (to the extent of 1·42 p. c. when prepared from the white of hen's eggs), Mulder's views underwent further modification (*Scheik. Onderz.* 4, 195; *J. pr. Chem.* 44, 488; *Kopp's Jahresber.* 1847 and 1848, 834).

According to these modified views, albuminous substances are compounds of protein. $C^{36}N^4H^{25}O^{10}$, or the protein-oxides, $C^{36}N^4H^{25}O^{11}$ and $C^{36}N^4H^{25}O^{13}$, with sulphamide, SNH^2, and phosphamide, PNH^2. On dissolving in potash-ley, there is formed on the one hand hyposulphurous acid (which was said to combine with protein in extremely variable proportions), with elimination of nitrogen and hydrogen, and on the other hand, hypophosphite of potash, with elimination of ammonia. These statements were equally without experimental foundation, and there now remains of Mulder's protein theory nothing but the name. In addition to the literature quoted, see Mulder's *Versuch einer allgemeinen physiologischen Chemie*, translated into German by Kolbe; further *Scheik. Onderz.* 3, 357; and *Chem. Untersuch.*, Frankfort, 1847. On the amount of sulphur in proteides in particular, see Rüling (*Ann. Pharm.* 57, 301, 315, and 317); Fleitmann (*Ann. Pharm.* 61, 121, and 66, 380); De Vrij (*Ann. Pharm.* 61, 248).

According to Leconte and Goumoens (*Compt. rend.* 36, 834; *Kopp's Jahresber.* 1853, 587) many albuminous substances consist of a portion soluble in acetic acid, and another portion insoluble therein, *Oxoluin* and *Anoxoluin*. These substances may even be distinguished under the microscope, in fibrin, as parallel fibres and as granulations.

When fibrin is treated with glacial acetic acid, it is converted into a colourless translucent jelly, in which the unaltered fibres are still recognisable. The fibres do not dissolve even after a month's digestion, and are rendered white and opaque again by potash. When the jelly is thrown on a filter, a colourless liquid runs through, which deposits dull-white flocks on neutralisation with potash.

Muscular fibre immersed in glacial acetic acid swells up, becomes transparent, and is resolved into a soluble and an insoluble portion. Albumin, casein, globulin, and vitellin behave in a similar manner.

Anoxoluin dissolves easily in dilute sulphuric acid with reddish colour; oxoluin dissolves partially only, with yellow colour. Similarly the former dissolves freely in warm hydrochloric acid, forming a fine violet solution; the latter colours the acid yellow without dissolving to any great extent. Boiling aqueous tartaric acid renders oxoluin transparent, and dissolves anoxoluin. A mixture of mercuric and mercurous nitrate colours anoxoluin carmine or vermilion-red, but scarcely affects oxoluin. The latter is not attacked by a mixture of chromate of potash and sulphuric acid at 100°, whilst anoxoluin is dissolved thereby with reddish-brown colour.

Gerhardt (*Traité* 4, 432) supposed albumin, casein, and fibrin to contain one and the same organic compound, which, as acid soda-salt, formed soluble albumin, as neutral soda-salt, casein, and when mixed with phosphates of the alkaline earths, fibrin. This view does not seem to be well-founded so far as regards fibrin, but it appears to express rightly to some extent the relation of albumin to casein. See **Casein.**

Sources of Proteides. They form the principal part of the organic compounds occurring in the blood, muscles, nerves, glands, and other organs and fluids of men and other animals, but are rarely found in normal urine, sweat, bile, tears, or other secretions, with the exception of milk. They occur also, though less abundantly, in all vegetable organs.

Some proteides are known to be conjugated compounds, by the decomposition of which simpler proteides are formed. Mucin, for instance, when boiled with acids, breaks up into acid-albumin and grape-sugar; hyalin yields a simpler body and grape-sugar; hæmoglobin yields hæmatin and sugar.

Properties. Most proteides are white, amorphous, flocculent or lumpy, inodorous, and tasteless. In the dry state they are for the most part yellow, brittle, horny masses. Those which are soluble in water are obtained in the form of yellow, transparent, shining masses on evaporating their solutions at low temperatures. In aqueous solution they always rotate polarised light to the left (Hoppe-Seyler). Danilewsky, however, mentions an optically inactive albumin.

Composition. Egg-albumin, serum-albumin, and casein contain approximately the same proportions of carbon, nitrogen, and hydrogen, viz., about 53·4 p. c. C., 15·8 N., and 7·1 H.: fibrin appears to contain more nitrogen (16·6 p. c.). The proportion of sulphur amounts to about 2 p. c. in egg-albumin, and about 1 p. c. in casein: serum-albumin and fibrin contain between 1 and 2 per cent. — Ossein, gelatin, hyalin, and some other proteides are free from sulphur. Hyalin is characterised by its low percentage of nitrogen (4·3 to 5·2 p. c.). Horn substance is rich in sulphur, which may amount, in hair, to as much as 8 per cent. Hæmoglobin and hæmatin contain iron; turacin contains copper as an essential constituent.

But few proteides are altogether free from ash: none of them are obtained free from ash in the soluble state. The ash of soluble albumin and casein contains carbonate of potash; that of fibrin does not.

Mulder supposed fibrin, egg-albumin and serum-albumin to contain phosphorus as an essential constituent. See Laskowski's comparison of Mulder's analyses (*Ann. Pharm.* 58, 138) in which, moreover, the sulphur was erroneously determined.

According to Liebig (*Chem. Briefe*, 3, Aufl. 574) the constituents of the animal body may be arranged in the following order, according to the proportion of carbon which they contain in combination with the same amount of nitrogen. To each atom of nitrogen there are present:—

8 atoms of carbon in egg-albumin, serum-albumin, flesh-albumin, flesh-fibrin, casein, and chondrin;
$7\frac{3}{4}$ atoms of carbon in blood-fibrin;
7 atoms of carbon in horn and hair;
$6\frac{1}{8}$ atoms of carbon in gelatinous tissue and membranes.

The analytical results which have been obtained, lead to the following empirical formulæ:—

Blood-albumin	$S^2N^{27}C^{216}H^{169}O^{68}$.
Flesh-albumin	The same
Syntonin	The same
Egg-albumin	$S^3N^{27}C^{216}H^{169}O^{68}$

Casein	$S^3N^{36}C^{288}H^{228}O^{90}$
Blood-fibrin	$S^2N^{40}C^{298}H^{228}O^{92}$
Chondrin	$N^9C^{72}H^{59}O^{32}$
Gelatinous tissue	$N^{13}C^{82}H^{67}O^{32}$.

The following relations are observable amongst these formulæ :—

Casein + 10 at. oxygen = chondrin + blood-albumin;
Albumin + 10 at. water = 2 gelatin + taurocholic acid;
Blood-fibrin + 8 at. water = blood-albumin + gelatin;
Chondrin = glycocoll + 2 uric acid + 8 water;
Gelatin + 10 at. oxygen = glycocoll + 3 uric acid + 12 water;
Albumin + 10 at. water + 56 at. oxygen = taurocholic acid + 2 glycocholic acid + 12 urea + 36 carbonic acid.

Many proteides, as egg-albumin, serum-albumin, casein, albuminic acid, paralbumin, syntonin, myosin, paraglobulin, and fibrin, when heated with water, yield *coagulated albuminous substances*, which are otherwise obtained for the most part by the prolonged action of alcohol. They behave with solvents like fibrin, but are hard and brittle, and do not swell up in saline solutions. — The rotatory action on polarised light of their solutions in soda-ley varies according to their origin (Hoppe-Seyler). Other methods of distinguishing the coagula of different proteides are wanting. — These coagula when boiled with water do not swell up, but retain their form, or give off flocks and detached fragments after some time only (Hoppe-Seyler, *Virchow's Archiv.* 5, 171).

Animal substances submitted to dry distillation, yield carbonic acid and combustible gases, a sublimate of carbonate of ammonia, a pale-brown aqueous liquid (*Spiritus Cornu Cervi*), and a black-brown tar (*Oleum Cornu Cervi*), and leave a difficultly combustible charcoal containing nitrogen.

The aqueous liquid contains carbonic, hydrosulphuric, hydrocyanic, and acetic acids in combination with ammonia; also empyreumatic oils and resins. — The tar yields by oft-repeated rectification, *Ol. animale Dippelii.* See Klauer (*Ann. Pharm.* 19, 135). Buchner (*Repert.* 61, 55). The tar obtained by the dry distillation of bones previously freed from fat (crude commercial *bone-oil*), is nearly black, and of sp. gr. 0·97. It gives up basic constituents to acids: strong acids in excess also dissolve from it an easily decomposible non-basic oil. Alkalis take up an acid oil and a large quantity of prussic acid. The vapour of the oils rapidly colours pine-wood soaked in hydrochloric acid, red, owing to the pyrrol which it contains. — Bone-oil yields by rectification: 1. A very volatile oil and water, holding in solution cyanide of ammonium and hydrosulphate and carbonate of ammonia, with small quantities of volatile bases. 2. Less volatile oils, which, as the boiling-point rises, become darker and thicker, and at last appear dark reddish-brown by reflected, and green by transmitted light. 3. Water and carbonate of ammonia formed by decomposition of the last portions; and finally a residue of charcoal. — The oil contains a basic and a neutral portion, the former of which contains methylamine, propylamine, butylamine, and probably higher members of the same series, besides pyrrol (xv, 5), petinine (xv, 159), pyridine (x, 406), picoline (xi, 263), lutidine (xii, 337), and collidine (xiii, 148). The non-basic portion contains a liquid boiling at 65·5°, which in the cold separates into two layers, one containing the alcohol-radicals of the fatty acids, and apparently also benzene and homologous hydrocarbons. On prolonged boiling with potash it evolves ammonia, and afterwards when supersaturated with sulphuric acid, emits the odour of butyric acid; it probably, therefore, contains nitriles (Anderson). See also Unverdorben (*Pogg.* 8, 253 and 477), who distinguishes in animal oil, animine, ammoline, odorine, fuscine, empyreumatic acid, resins, and neutral animal oil. The residual coke when formed at low temperatures, contains about 5·7 per cent. of nitrogen. After subjection to a bright-red heat it contains from 2·5 to 3·1 per cent. (Fleck, *Fabrik. chem. Prod. aus thier. Abfällen*, 1862, 15). — When horn or fish is submitted to dry distillation, and the products are passed over heated soda-lime, no nitrogen is evolved; neither is any product formed capable of yielding ammonia by treatment with soda-lime (Schlun, *N. Br. Arch.* 111, 11).

Owing to the nitrogen which they contain, horny tissue, gelatin, chondrin, chitin, and albuminous substances, when introduced into the point of a *blowpipe-flame*, colour it distinctly green at the edges, with a reddish centre (Vogel & Reischauer, *N. Repert. Pharm.* 5, 153; *Kopp's Jahresber.* 1856, 752).

When proteides are submitted to prolonged boiling with *water*, in contact with the air, or when they are heated to temperatures between 108° and 200° with water in sealed tubes, easily soluble products are obtained. Mulder described these products as protein oxides. Meissner obtained peptones and other bodies from syntonin and casein. W. Schmidt, who employed a higher temperature than Meissner, found no peptone. See egg-albumin, fibrin, casein, serum-albumin, syntonin, and paraglobulin.

On digesting protein (the precipitate thrown down by acids from alkaline solutions of the proteides) in *oil of vitriol* for 24 hours, it swells up to a jelly, which, when immersed in water, shrinks to a white insoluble mass. When washed with water and purified by boiling with alcohol and dried, this mass, Mulder's *protein-sulphuric acid*, is hard and white, and does not redden litmus. It forms soluble compounds with the alkalis and with baryta and lime, and insoluble compounds with the oxides of the heavy metals. It contains 50·94 p. c. C., 15·08 N., 6·93 H., 18·74 O., and 8·34 SO^3, and is represented by the formula $2C^{36}N^4H^{27}O^{12},SO^3$ (Mulder, *Berzel. Jahresber.* 19, 642; 23, 600).

Proteides submitted to prolonged boiling with *hydrochloric acid* or moderately dilute *sulphuric acid* yield crystalline products, amongst which leucine and tyrosine are the most common.

Of crystalline products, elastic tissue yields leucine only; gelatinous tissues yield leucine and glycine; albumin, casein, and fibrin yield leucine with a little tyrosine; horny tissue and animal mucus yield leucine with 4 p. c. or more of tyrosine. Fibroïn gives 5 to 8 p. c. of tyrosine, together with leucine and glycine. Sericin yields tyrosine, leucine, and serine (Städeler). Legumin yields, besides tyrosine and leucine, glutamic and aspartic acids; the latter acid is also obtained from egg albumin (Ritthausen). See also Mulder (*J. pr. Chem.* 21, 343), who obtained humic acid and ammonia by boiling protein with hydrochloric acid.

Proteides digested with *nitric acid* form a pale lemon-yellow powder, which when washed with water leaves dark-yellow xanthoproteic acid. The pale-yellow body forms with lime an insoluble salt of xanthoproteic acid and soluble salts of nitric and saccharic acids, so that it probably contains these acids in combination (Berzelius, *Jahresber*, 19, 651). See also Xanthoproteic acid, p. 264.

On warming the liquid white of hens' eggs, glutin, or flesh with a mixture of 2 volumes of fuming *nitric acid* and 1 volume of strong *hydrochloric acid*, a violent frothing and evolution of nitric oxide takes place, and decomposition-products are formed, part of which pass over in the acid fumes, another portion separating from the acid solution on cooling, while a third portion remains dissolved. A very large excess of nitric acid destroys the products thus formed, and there remains, instead of them, only a small quantity of volatile crystals and a large quantity of oxalic acid.

To obtain these products, one of the proteides is dissolved in warm fuming nitric acid, with addition of water if necessary, and the solution is filtered, mixed with half its volume of strong hydrochloric acid, and distilled till the contents of the rètort throw down a yellow waxy tough mass.

a. Oily drops of chorazol pass over with the acid vapours. They collect at the bottom of the receiver, and are afterwards purified by distillation with water and dried over chloride of calcium.

Chlorazol is a thin yellow oil, of sp. gr. 1·555, having a very powerful odour and an acid reaction, and acting as a poison. It explodes violently when heated. Dissolves very sparingly in water and does not take up water, but when it is left in contact therewith, its surface acquires a dull-white appearance. Dissolves freely in alcohol. — When this chlorazol, obtained by the treatment of the original proteide, is distilled alone, an evolution of hyponitric acid takes place, and at about 140° there passes over an oily body (*b*) resembling chlorazol but differing in composition and having the sp. gr. 1·628. Lastly, the non-volatile decomposition-products obtained in the first operation (see below) yield, by repeated treatment with nitric acid, oily bodies (*c* and *d*) [illegible] lorazol.

Analyses by Mühlhäuser.

	a.	*a.*	*b.*	*b.*	*c.*	*c.*	*d.*	*d.*
C	18·91	19·44	12·77	13·98	12·03	12·78	13·05	13·2
H	1·72	2·90	1·19	1·75	1·07	1·13	0·70	0·8
Cl	40·19	44·98	56·88		38·40	38·50	36·80	
N	11·80				13·10	15·70	7·80	

Calculations, according to Mühlhäuser.

a.		*b.*		*c.*		*d.*	
8 C	19·23	4 C	13·44	4 C	12·70	4 C	12·6
3 H	1·20	2 H	1·12	2 H	1·06	H	0·52
3 Cl	42·68	3 Cl	59·66	2 Cl	37·6	2 Cl	37·36
2 N	11·22	N	7·84	2 N	14·8	N	7·3
8 O	25·65	4 O	17·81	8 O	33·8	10 O	42·2
$C^{8}Cl^{3}X^{2}H^{3}$	100·00	$C^{4}Cl^{3}XH^{2}$	100·00	$C^{4}Cl^{2}X^{2}H^{2}$	100·00	$C^{4}Cl^{2}XHO^{6}$	100·00

Strecker (*Handwörterb.* 2 Aufl. 2, 2, 166) regards *a* as a mixture, and *c* and *d* as essentially identical, probably having the composition *c.* On this supposition both bodies are homologous with chloropicrin (xi. 216).

b. The residue in the retort deposits on cooling a large quantity of a transparent syrupy body, the quantity of which is increased by mixing it with water, then driving off most of the acid with addition of alcohol, and again mixing with water. It is purified by boiling with water.

This *second body* forms an acid liquid of the consistence of turpentine, which turns red in the air, smells of bitter almond oil, and tastes bitter. Sp. gr. 1·36. When heated it becomes thinner, turns brown and decomposes, without exploding. It is nearly insoluble in water, but when boiled persistently with water it loses chlorine. When treated with potash, it gives up part of its nitrogen in the form of ammonia: acids throw down from the solution a body resembling the original. — It dissolves easily in alcohol and less freely in ether.

Calculation, according to Mühlhäuser.			Mühlhäuser.
24 C	144	42·29	40·05 to 43·56
12 H	12	3·52	3·30 to 5·33
3 Cl	106·5	31·28	29·23 to 34·43
N	14	4·11	4·22 to 4·24
8 O	64	18·80	
$C^{24}Cl^3XH^{12}O^4$	340·5	100·00	

The second body undergoes further decomposition when it is distilled with 100 parts of fuming nitric acid. Chlorazol (*c*) then passes over, and the residue deposits *crystals*, while an *amorphous body* remains in solution. No oxalic acid is produced. — The crystals are white loose needles, having an odour of benzoic acid and a sour taste; they are fusible and susceptible of sublimation, and are represented by the formula $C^{14}Cl^2H^4O^6$. They dissolve easily in hot nitric acid and are deposited from the solution unchanged as it cools. — The amorphous body is semi-fluid, ropy, strongly acid, inodorous, very hygroscopic, and has the composition represented by the formula $C^{12}Cl^2XH^3O^2$. It volatilises in irritating vapours without leaving a residue; dissolves slightly in water and easily in aqueous alkalis, with which it forms crystallisable salts.

c. After the removal of the chlorazol and the second body, there remain in the mother-liquor, sulphuric, oxalic, and fumaric acids (x, 22), and a non-volatile *third body*. Excess of the acids employed is driven off; the oxalic acid is allowed to crystallise; and the thick residue is mixed with 3 or 4 times its volume of water, whereupon the third body is precipitated and collects in the form of a heavy oily layer. The mother-liquor contains salts of fumaric and sulphuric acids.

The *third body* is a thin oil of brown-red or paler colour, an agreeable aromatic odour, and acid reaction. It forms an opaque solid in the cold, and burns without explosion. It dissolves slightly in water, sparingly in aqueous ammonia, and easily in alkalis. The alcoholic solution throws down from metallic salts coloured amorphous precipitates, which lose organic matter on drying. It dissolves freely in alcohol.

Calculation, according to Mühlhäuser.			Mühlhäuser. *Dried in vacuo over oil of vitriol.*	
26 C	156	35·57	35·52	35·4
18 H	18	4·11	4·40	4·3
3 Cl	106·5	24·28		23·42
N	14	3·20	3·2	
18 O	144	32·84		
$C^{26}Cl^3XH^{18}O^{14}$	438·5	100·00		

When distilled with fuming nitric acid, this third body likewise undergoes decomposition, by which chlorazol, (*d*) volatile acids (among which valerianic acid predominates), crystals, and an oily body are produced, but no oxalic acid.

The *crystals* are obtained in small quantity only. They form inodorous short white needles, fusible, and volatilisable in irritating vapours. They dissolve with difficulty in hot water, easily in alcohol, and are represented by the formula $C^{16}Cl^{2}H^{6}O^{4}$. The potash-salt contains 20·51 p. c. of potash.

The *oil* is of a clear pale-yellow colour, nearly inodorous, bitter, and very acid. It volatilises in white vapours, apparently undecomposed. The compounds with bases are amorphous, brownish-red or orange. The oil dissolves sparingly in water, easily in alcohol (Mühlhäuser, *Ann. Pharm.* 90, 170; 101, 171).

Calculation, according to Mühlhäuser.			Mühlhäuser. *Dried at* 100°.	
24 C	144	33·9	33·24	33·11
16 H	16	3·8	4·05	3 9
3 Cl	106·5	25·0	25·0	24·77
N	14	3·4	3·3	3·3
18 O	144	33·9		
$C^{24}Cl^{3}XH^{16}O^{14}$	424·5	100·0		

Albumin, fibrin, casein, and wheat-gluten, treated with a mixture of *binoxide of manganese* and *sulphuric acid*, or of *bichromate of potash* and *sulphuric acid*, yield liquid fatty acids, benzoic acid, and the aldehydes of these acids; with bichromate of potash, prussic acid and valeronitrile are also formed. See further particulars under Casein.

Solid albuminous substances are coloured blue by sulphuric acid containing *molybdic acid* (Frohde, *Ann. Pharm.* 145, 376; *Chem. Centr.* 1868, 640).

All albuminous substances (as, for example, egg and serum albumin, the substance precipitated by acetic acid from blood-serum, alkaline solution of fibrin to which enough acetic or phosphoric acid has been added to redissolve the precipitate first thrown down) are precipitated from their solutions in acetic acid by *neutral salts*, such as chloride of sodium, acetate of soda, phosphate of soda, chloride of calcium, or sulphate of magnesia. A similar behaviour is exhibited in solutions containing excess of phosphoric, oxalic, lactic, or tartaric, instead of acetic acid. The precipitation takes place with especial facility when the acid solution is heated and cooled again before adding the neutral salt; it is effected the more easily the higher the temperature and the stronger the solution. On dissolving serum-albumin, coagulated by heat, in very dilute potash-ley, adding acetic acid till the precipitate at first produced disappears, and then mixing the liquid with an equal volume of an aqueous solution of sulphate of magnesia, the mixture remains clear at 13°, becomes slightly turbid at 15° to 16°, more so at 19°, and throws down dense flocks at 32°. 100 parts of a solution of serum-albumin in phosphoric acid, when mixed with 1 part of a solution of chloride of sodium, do not become turbid even on boiling; 6 parts of the salt solution cause turbidity at 50°, 8 parts at 27°, and 10 parts at 19°. Acetic and phosphoric acid solutions of egg- and serum-albumin and of fibrin, behave in the same manner; coagulated egg-albumin dissolved in acids is precipitated only at higher temperatures, or by a larger proportion of neutral salts, than serum-albumin.

The precipitates thus formed, Panum's *acidalbumin*, exhibit the following reactions. After the removal of salts, they dissolve in water, especially in very cold water, forming solutions which are not coagulated by heat; they lose this property, however, when dried in the air, or when heated with saline solutions. Before they are altered by exposure to air, they dissolve in excess of acetic or phosphoric acid, and sometimes in cold or warm alcohol. Their aqueous solutions are precipitated by ferrocyanide of potassium, an excess of which redissolves the precipitate, whereas solutions of albumin are precipitated by ferrocyanide of potassium only after addition of acetic acid, and the resulting precipitate is insoluble in excess of the precipitant (Panum, *N. Ann. Chim. Phys.* 37, 237 ; *J. pr. Chem.* 59, 55).

When white of egg is diluted with an equal volume of water and filtered, and the filtrate is saturated with neutral salts, solutions are obtained (albumino-saline solutions) which behave as follows :

They are precipitated by tribasic phosphoric acid, except when the salt added is borax, phosphate of soda, acetate of potash, or acetate of soda. The precipitates are granular, and soluble in excess of phosphoric acid. — They give with acetic acid, granular or flocculent precipitates, which are insoluble in excess of acetic acid, and dissolve in phosphoric acid only when they are granular; this last solution is again precipitated by excess of acetic acid. The precipitates produced by acetic acid are insoluble in ammonia, either cold or warm, and in cold strong potash solution (Melsens). For the behaviour with corrosive sublimate see egg-albumin.

When the solutions used in these reactions are so dilute that no precipitates are produced, fibres make their appearance in them on stirring, which fibres afterwards unite to form membranes (Melsens). On the behaviour of albumin with very dilute hydrochloric acid and chloride of sodium, see Arnold (*Schmidt's Jahrb.* 103, 1).

According to Eichwald (*Chem. Centr.* 1869, 565) these precipitates consist of mixtures of paraglobin and syntonin in varying proportions, according to the kind and quantity of the acid contained in them. When to a mixture of equal volumes of serum and saturated solution of chloride of sodium, so much hydrochloric acid is added that 100 c.c. of the mixture contain from 0·5 to 1·0 gramme of hydrochloric acid, and the mixture is filtered after standing for a day or longer, the resulting precipitate forms with water a strongly acid solution, from which soda, or carbonate of soda, added till the reaction is very feebly acid, gradually throws down syntonin, whilst coagulable paraglobin remains in solution. If, on the contrary, the precipitate be freed from adhering acid, by washing it with a half-saturated solution of chloride of sodium, water then dissolves the paraglobin (owing to the presence of chloride of sodium) and leaves the syntonin undissolved. The only peculiarities exhibited by the paraglobin contained in the precipitate are, that it does not lose its coagulability, and is not converted into syntonin, even on standing for months in a solution containing much hydrochloric acid, as would be the case with paraglobin alone in contact with hydrochloric acid. — When acetic acid is used to precipitate the mixture of serum and chloride of sodium, the precipitate is perfectly soluble in water, even after washing with chloride of sodium (Eichwald).

When serum, previously freed from paraglobin and diluted with ten times its bulk of water, is mixed with so much acetic acid that it no longer coagulates on boiling, but is completely precipitable by ferrocyanide of potassium, and then with its own volume of a saturated solution of chloride of sodium, syntonin is thrown down as a greyish-white precipitate, which slowly contracts to a dense mass. When this precipitate is freed from excess of acid by washing with a half-saturated solution of chloride of sodium, water first takes up part of the chloride of sodium, and then dissolves the precipitate itself. The solution has a faint acid reaction, coagulates partially on boiling, and completely after addition of a small quantity of carbonate of potash, whilst excess of alkali prevents coagulation. The solution is precipitated by strong mineral acids; the precipitate produced by nitric acid is nearly insoluble in excess of the precipitant, but that produced by sulphuric acid is completely soluble. The solution is precipitated also by neutral acetate of lead, corrosive sublimate, tannic acid, and cupric sulphate, the precipitate produced by the last being soluble in excess (Eichwald).

Strong *potash-ley* produces with albuminous substances the bodies hereafter described as albuminates (Mulder's protein). These bodies resemble one another in their behaviour towards reagents, but exhibit some differences amongst themselves in their action on polarised light.

Albumin, casein, and fibrin, treated with fused *hydrate of potash*, yield volatile ammoniacal products, leucine, tyrosine, volatile acids, and non-crystallisable substances.

Solutions of proteides (albumin, fibrin, casein, glutin, legumin) in potash yield iodoform when treated with *iodine* and *bicarbonate of potash* (Millon, *Compt. rend.* 21, 828; *J. pr. Chem.* 37, 53).

Liquids containing albumin, fibrin, casein, or gelatin assume, on addition of potassio-cupric tartrate, a fine violet colour like that of permanganate of potash. This colour is produced with very small quantities of the albuminous substances, at least on heating. Acids decolorise the solution, whereas alkalis restore the colour (Humbert, *N. J. Pharm.* 27, 272; *Kopp's Jahresber.* 1855, 825). Solid albuminous substances and their derivatives assume a deep violet-blue colour when moistened with cupric sulphate and then with potash (Piotrowski, *Wien. Acad. Ber.* 24, 335; *Kopp's Jahresber.* 1857, 534). The skin of the finger, feathers, silk, gelatigenous substances, yeast, and sponge, likewise exhibit the violet coloration when moistened with cupric nitrate and soda-ley (A. Vogel & Reischauer, *N. Repert.* 8, 529; *Kopp's Jahresber.* 1860, 566). Ritthausen (*J. pr. Chem.* 85, 208; 99, 449; 102, 376) adds to the acetic solution of the albuminous substance a little cupric sulphate, and then potash-solution, whereupon, if albumin, casein, or legumin is employed, the violet colour appears. On dropping the cupric sulphate into the alkaline solution and shaking, the precipitate formed at first is redissolved with violet colour. In presence of dextrin or sugar, the solution is coloured blue, without any precipitate of cuprous oxide being formed. See also under Egg-albumin.

Protein substances (albumin, fibrin, casein, silk, wool, gelatin, horn) added to a solution of 1 part of *mercury* in 1 part of *nitric acid* and 4½ parts of *water*, produce an intense red coloration, which is increased by warming. This is the case not only with the undissolved substances, but also with their aqueous solutions, and more especially with solutions in alkalis or sulphuric acid. Neither mercurous nitrate nor mercuric nitrate produces this coloration, except in presence of nitrous acid (Millon, *Compt. rend.* 28, 40; *Ann. Pharm.* 72, 349). A solution of mercuric oxide in nitric acid, not in excess, colours albuminous substances orange (not red) on boiling, but after addition of a few drops of highly diluted fuming nitric acid, the colour produced is a dark purplish-red. The white precipitate produced on boiling albumin with the mercuric solution likewise turns red on warming it, after washing and drying, with a trace of impure nitric acid (Kühne & Rudneff, *Virchow's Arch.* 33, 71; *Anal. Zeitschr.* 4, 449). See also Lassaigne & Labaillef (*Ann. Chim. Phys.* 45, 435) who consider the presence of both mercurous and mercuric salt to be necessary.

In contact with *oil of vitriol* and *sugar*, the protein substances albumin, casein, and globulin, and likewise the vegetable proteides, exhibit a red coloration; the gelatigenous tissues, under the same circumstances, acquire a dirty yellowish-red colour; chondrin, glutin, and elastic fibre remain uncoloured. When the white of hens' eggs is diluted with 5 parts of water, and oil of vitriol is gradually added to the filtrate till the precipitate produced at first is redissolved, the further addition of a few drops of a solution of cane-sugar produces a red to deep-violet coloration, which becomes most intense in a quarter of an hour. Ammonia (not in excess) throws down from the solution violet flocks which, after washing, dissolve in oil of vitriol with purplish-red, and in dilute sulphuric acid with violet-red colour. These flocks are coloured violet by hydrochloric acid, and yellow by nitric acid; they dissolve in potash and ammonia (M. S. Schultze, *Ann. Pharm.* 71, 266). See also xv, 322 and xviii. Koschlakoff & Bogomoloff (*Anal. Zeitschr.* 7, 514) distinguish these reactions from the similar reactions of the bile-acids by means of the spectroscope.

Gastric juice, either artificial or natural, dissolves most proteides at 30° to 45°, forming syntonin and lævorotatory peptones, which are not thrown down by boiling with water. — On the putrefaction of proteides, see more particularly Casein.

On the behaviour of proteides with *diastase*, see Mulder (*Scheik. Verhandel. en Onderzoek.* 2 *Deel*, 2 *Stuk*, *Onderzoek.* 130; *Kopp's Jahresber.* 1858, 536): on their behaviour with *pigments*, see Maschke (*J. pr. Chem.* 76, 37).

2. *Mulder's Derivatives of Protein Substances.*

a. Protein-oxide or *Oxyprotein.* — Formed when chlorite of protein is dissolved in aqueous ammonia.

This solution, the formation of which is attended with the evolution of a large quantity of nitrogen, leaves on evaporation a residue soluble in hot water, from which boiling alcohol precipitates oxyprotein, whilst chloride of ammonium remains in solution.

Oxyprotein is a yellow powder which cannot be obtained free from chlorine, even by repeated boiling with alcohol. It is soluble in water, and the solution gives with sulphuric acid a white precipitate, which disappears on heating. It dissolves in strong hydrochloric acid, forming a solution which turns brown when heated. Nitric acid converts it into xanthoproteic acid. It is dissolved by ammonia, alkalis, and baryta-water. The aqueous solution is not affected by ferrocyanide of potassium, but is precipitated by infusion of galls, and by salts of silver, lead, iron (ferric salt), and copper; the precipitate formed by acetate of copper contains 3·64 p.c. CuO. Oxyprotein is insoluble in alcohol and ether. It contains, on the average (as prepared from albumin or casein), 50·18 p.c. C., 6·67 H., 15·12 N., and 0·5 Cl. (Mulder, *J. pr. Chem.* 20. 340).

Van Laer (*Scheikund. Onderzoek* 2, *Stuk.* 75; *Berzel. Jahresber.* 23, 617), who prepared oxyprotein with proteinchlorous acid from hair, found 51·62 p.c. C., 6·67 H., and 15·07 N. On his bioxyprotein from hair, see *Horn-substance.*

Subsequently (*Berzel. Jahresber.* 23, 595) Mulder regarded this decomposition-product of proteinchlorous acid as identical with substances which he found in the animal body, and also prepared from albumin and fibrin, and then described it as *trioxyprotein*, *hydrate of trioxyprotein*, or *bioxyprotein.*

The oxyproteins occur in the blood, especially in that of the arteries, and in *Crusta inflammatoria.* They are produced from fibrin by assimilation of oxygen, which takes place either at ordinary temperatures or on boiling with water, with access of air. Yeast contains a body which may be converted into proteinchlorous acid and trioxyprotein. Pyin is trioxyprotein (*Berzel. Jahresber.* 24, 711): boiled flesh contains a mixture of bioxyprotein and fibrin.

When fibrin is submitted to prolonged boiling with water in contact with the air, the portion remaining undissolved consists of bioxyprotein; on evaporating the solution to dryness and treating the residue with alcohol, trioxyprotein remains behind. — Trioxyprotein is $C^{36}N^{4}H^{25}O^{13}$ or $C^{40}N^{5}H^{32}O^{16}$; its copper-compound is $C^{40}N^{5}H^{31}CuO^{16} + C^{40}N^{5}H^{32}O^{16}$. According to Schröder (*Scheik. Onderz.* 3, *Stuk.* 259; *Berzel. Jahresber.* 23, 598), the lead- and silver-compounds have a corresponding composition. — When trioxyprotein is dissolved in potash and precipitated by a current of chlorine, the precipitate consists of trioxyproteinchlorous acid, from which ammonia again produces trioxyprotein (Mulder, *Berzel. Jahresber.* 23, 595. — *Scheik. Onderz.* 1, 550; *Ann. Pharm.* 47, 300; *Berzel. Jahresber.* 24, 654. — *J. pr. Chem.* 44, 501).

Hoppe-Seyler (*Virchow's Arch.* 5, 171), by boiling dried serum-albumin with water, under a pressure of 3 atmospheres, obtained a turbid liquid behaving like Mulder's trioxyprotein. The epidermis of *Trepidonotus natrix*, freed from connective tissue, yields by the same treatment protein-oxide or a similar body. These bodies are therefore formed without assimilation of oxygen (Hoppe-Seyler).

β. Xanthoproteic acid. — Previously noticed by Fourcroy & Vauquelin and by Berzelius (p. 258). — Produced by the action of nitric acid on protein-compounds.

Mulder digests in nitric acid for 24 hours, protein previously soaked in water; dilutes; filters; washes the resulting lemon-yellow powder till it becomes dark-yellow, whereby excess of nitric acid is got rid of; then dries, and frees the product from fat by boiling with alcohol and water.

Xanthoproteic acid thus prepared is an orange-yellow powder containing, on the average, 50·37 p.c. C., 6·60 H., 14·00 N., and 27·99 O. It dissolves slowly to a red jelly in oil of vitriol; and from this jelly water throws down a compound of xanthoproteic acid with sulphuric acid, from which water removes the whole of that acid. — The solution in nitric acid is rendered colourless by boiling, with formation of oxalic acid. The yellow solution in hydrochloric acid leaves on evaporation a brown deliquescent mass. — Xanthoproteic acid evolves ammonia when boiled with excess of potash. It dissolves in ammonia, forming a solution which, when evaporated, leaves the acid free from ammonia. Chlorine passed into the red ammoniacal solution decolorises it and throws down yellowish-white flocks, which are lemon-yellow after drying; according to Mulder, they contain chlorous acid, and yield xanthoproteic acid when again treated with ammonia. — The acid is insoluble in water, alcohol, and ether. It dissolves in nitric acid, and is precipitated from the solution by water. It forms a dark-red neutral salt with potash; neutral and acid salts of the heavy metals; and an insoluble lime-salt (Mulder, *Berzel. Jahresber.* 19, 561. — *J. pr. Chem.* 20, 352).

Van der Pant (*Scheikund. Onderzoek.* 5, 2 *Stuk.* 136; *Kopp's Jahresber.* 1849, 507) obtained xanthoproteic acid of nearly the same composition from albumin, cow-horn, horse-hoofs, blood-fibrin, cheese, wool, horse-hair, and protein from albumin or horn, by submitting these bodies to more or less prolonged digestion with nitric acid, washing the undissolved residue, treating it with ether, and drying at 130°. It forms an ammonia-salt which is decomposed at 130°, leaving unchanged xanthoproteic acid; a soluble baryta-salt containing 12·7 to 13·1 p. c. BaO; a green, insoluble copper-salt containing 12·9 p. c. CuO; and a yellow, insoluble lead-salt containing 14·0 p. c. PbO.

Xanthoproteic acid, according to van der Pant.

	From albumin.	From horn.	From horse hoofs.	From fibrin.	From cheese.	From wool.	From hair.	From protein.	
C	50·3	50·1	49·5	49 3	50·7	49·4	49·2	50·9	50·6
H	6·4	6·2	6·5	6·2	6·3	6·4	6·0	6·6	6·4
N	14·8	14·8	14·1	14·8	14·4	14·5	14·7	14·8	14·7
O	27·3	27·2	28·4	28·3	27·8	28·7	28·0	26·2	28·2
S	1·1	1·7	1·3	0·9	0·9	0·8	1·9	1·5	
Ash	0·1	0·1	0·2	0·4	0·2	0·1			

γ. *Proteinchlorous acid.* — When chlorine is passed into diluted and filtered white of hens' eggs, or into a solution of casein or fibrin in ammonia not in excess, white flocks are produced which, according to Mulder's earlier statements (*Berzel. Jahresber.* 19, 734; *J. pr. Chem.* 20, 340), consist of proteinchlorous acid. It was afterwards stated by Mulder (*Scheik. Onderz.* 4, 195; *J. pr. Chem.* 44, 489) that chlorine throws down from albumin, first chlorite of albumin, which produces sulphide of silver with silver-salts, and afterwards proteinchlorous acid, the sulphur of which no longer acts upon silver.

The flocks are to be washed so long as the wash-waters exhibit an acid reaction, up to which point silver-salts are still precipitated thereby, in consequence of the proteinchlorous acid being slightly soluble in water. — The acid is obtained of constant composition by drying at 80°, at which temperature water and chlorous acid are given off, then at 100°. Straw-yellow powder, which when heated swells up, melts, and evolves odorous gases. It is nearly insoluble in water and quite insoluble in alcohol and ether.

	Mulder.		van Laer.	
	From albumin.	*From fibrin.*	*From casein.*	*From hair.*
C	48·00	48·20	48·48	48·40
N	14·11			14·09
H	6·21	6·16	6·38	6·08
ClO^3	11·44	11·56	12·27	12·61

The body contains also 1·57 p. c. of sulphur (Kemp, *Ann. Pharm.* 60, 104). Van Laer (*Scheikund. Onderz.* 2, *Stuk.* 75; *Berzel. Jahresber.* 23, 617) obtained his proteinchlorous acid by treating clean human hair for a week with chlorine under water, whereby it was bleached, but still retained its form. — Proteinchlorous acid is not obtained by the action of chlorous acid on albumin (De Vrij, *Ann. Pharm.* 61, 248); moreover, the presence of chlorous acid in it has not been proved; neither is it probable.

Proteinchlorous acid dissolves in oil of vitriol, forming a colourless solution, from which water throws down white flocks. It dissolves slowly in nitric acid, without forming xanthoproteic acid; and in hydrochloric acid after some days, forming therewith a colourless liquid. — On dissolving it in ammonia, a large quantity of nitrogen is evolved, and the solution contains chloride of ammonium and trioxyprotein.

On dissolving proteinchlorous acid in baryta-water, removing excess of baryta by means of carbonic acid, and precipitating the solution with alcohol, the barium-salt of Mulder's *chloroxyproteinic acid* is formed, together with chloride of barium. The acid forms insoluble salts with cupric and ferric oxides. The baryta-salt contains 44·24 to 45·87 p. c. C., 5·75 H., 1·70 Cl., and 11·69 BaO., besides nitrogen and oxygen. The copper-salt contains 3·48 to 3·87 p. c. CuO.; the ferric salt 2·37 p. c. Fe^2O^3. (Mulder, *J. pr. Chem.* 20, 340).

3. *Individual Protein Substances.*

Myosin.

W. Kühne. *Untersuchungen über das Protoplasma und die contractile Substanz.* Leipzig, 1864, 2. — *Lehrbuch der physiologischen Chemie,* Leipzig, 1866, 272.

Discovered and investigated by Kühne.

Forms one of the chief constituents of the juice of muscles coagulated by *rigor mortis.* — Muscle-plasma, *i.e.*, the fluid contents of the elastic sheath of striped muscular fibre (the sarcolemma), when dropped into water, breaks up into myosin, which is precipitated, and muscle-serum, which remains in solution (Kühne).

The yolk of eggs, the crystalline lens, and the fluid of some cysts contain albuminous substances, insoluble in water, soluble in not too strong solutions of chloride of sodium, and probably identical with myosin; but it is not possible to precipitate them from their solutions by saturation with chloride of sodium (Hoppe-Seyler, *Anal. Zeitschr.* 3, 429).

Preparation of Muscle-plasma. — Owing to the speedy occurrence of *rigor mortis* in warm-blooded animals, the muscle-plasma can be obtained in an unaltered state only from cold-blooded animals, and by the employment of intense cold. The animals (frogs are the best) are bled to death, and a solution of common salt containing 0·5 per cent. is injected into the aorta, till colourless liquid flows from the veins. The muscles are then detached in such a manner that only the tendons are cut, washed with the same salt-solution, cooled to 0°, to remove the lymph still contained in them, and then exposed to the temperature of − 7°, until they can be cut into fine shavings with a cooled knife. These shavings are triturated to a snow-like powder in a cooled mortar, tied up in strong linen, and placed in a press at the ordinary temperature. The frozen mass thaws below 0°, and as it does so, the muscle-plasma flows away, and may be filtered, though with difficulty, by employing cooled funnels and filters wetted with ice-cold solution of salt.

Muscle-plasma thus obtained is a syrupy, not ropy but limpid, distinctly alkaline liquid, remaining fluid for a long time below 0°, but coagulating in two or three hours at ordinary temperatures, and immediately at 40°, to a solid gelatinous mass, which is resolved by pressure into myosin which remains behind, and muscle-serum which flows away. Solution of sodium chloride and very dilute acids also cause muscle-plasma to coagulate instantaneously.

To prepare myosin, the muscle-plasma is slowly dropped into water, whereupon each drop solidifies to an elastic globule, and the precipitate is washed with water. Or flesh, previously washed with water and chopped fine, is triturated with common salt to a pulp, which is diluted with so much water that the solution contains 10 per cent. of salt, and allowed to stand at the temperature of 24°, then pressed through linen and filtered. From the yellow syrupy filtrate thus obtained water precipitates the myosin.

Myosin is neutral after washing with water. In neutral or slightly acid solution it decomposes peroxide of hydrogen in the cold; at 55° the decomposition is less rapid, and at 60° it ceases altogether (Gianuzzi, *Virchow's Arch.* 34, 443). It is insoluble in *water*, but easily soluble in very weak *acids*, so that the globules of myosin formed on dropping muscle-plasma into hydrochloric acid containing 0·1 p. c. dissolve in the liquid on agitation (Kühne). Its solutions, when heated, coagulate the more easily the more acid they contain (Hoppe-Seyler). When thus dissolved, the myosin passes into syntonin, though only gradually, the precipitate produced by carbonate of soda in a freshly-prepared solution still containing myosin, while that produced in a solution which has been prepared some time consists solely of syntonin (Hoppe-Seyler). Myosin dissolves in very weak solutions of caustic *alkalis* and their carbonates, and in *lime-* and *baryta-water*, being thereby converted into albuminate. It dissolves very easily in solutions of *sodium chloride* containing 5 to 10 per cent. of the salt, and is precipitated therefrom on dilution with water; on saturating the solution with powdered salt, the myosin separates unaltered. and rises to the surface in flocks (Denis, Kuhne). The chloride of sodium solution of myosin does not coagulate when kept, but when heated to 55° or 60°, it deposits altered myosin, which no longer dissolves in chloride of sodium solution, scarcely swells up in hydrochloric acid of 0·1 p. c., and is converted thereby into syntonin only after long standing and heating (Kühne). The solution is coagulated by alcohol (Hoppe-Seyler).

The liquid expressed from the pulped muscle is Kühne's muscle serum. It may be obtained also by exhausting with water muscles free from blood in the state of *rigor mortis*, and it remains in solution when muscle-plasma is dropped into water, and the resulting myosin is separated by filtration.

The serum has an alkaline or neutral reaction when the pulp is made very quickly, but becomes acid on standing for a few hours at ordinary temperatures. It contains a compound of albuminate of potash with phosphate of soda, besides two other albuminous substances, and on this account coagulates either at 25° to 30°, in presence of a large quantity of free acid, or at 45° when alkaline, neutral, or but slightly acid; in either case there remains in solution some albumin, which coagulates at about 75° (Kühne, *Untersuch.* 12).

Syntonin.

LIEBIG. *Ann. Pharm.* 73, 125; *Pharm. Centr.* 1850, 269; *Chem. Gaz.* 1850, 169; *Kopp's Jahresber.* 1849, 489.
LEHMANN. *Physiolog. Chemie.* 2, Aufl. 1, 345.
KÜHNE. *Untersuchungen über das Protoplasma*, Leipzig, 1864, 15.
HOPPE-SEYLER. *Anal. Zeitschr.* 3, 428; *Krit. Zeitschr.* 1864, 737; *Kopp's Jahresber.* 1864, 615.
EICHWALD. *Würzburg. medic. Wochenschrift*, 5, 356; *Petersb. med. Zeitschrift*, 15, 239; *Chem. Centr.* 1859, 561.

Fibrin of muscular fibre, Muscle-fibrin, Musculin. Discovered by Liebig; named by Lehmann. Kühne showed that syntonin does not exist ready-formed in fresh alkaline muscular fibre, but is formed from the myosin contained therein.

Formation. By dissolving myosin (p. 266) in very dilute hydrochloric acid (Kühne). The flesh-fibres of poultry and of the ox yield almost exclusively syntonin; mutton contains more, and veal much more than half its weight of substances insoluble in hydrochloric acid, which are elastic, white, and softer and more gelatinous than soaked blood-fibrin (Liebig). Lehmann obtained syntonin from the smooth muscles of the stomach, intestines, and bladder, and from almost all contractile tissues.

At the present time, in accordance it would seem with Kühne's precedent, the products resulting from the action of dilute acids on soluble or coagulated albuminous substances and on fibrin are all reckoned as syntonin. According to Hoppe-Seyler, water throws down hydrochlorate of syntonin from solutions of all albuminous substances in strong hydrochloric acid.

Syntonin occurs in blood (Eichwald); in the fluid of the stomach, probably as the first product of the action of the gastric juice on albuminous substances. In artificial digestion it is formed before peptones. See further under Serum-albumin and Peptones.

Bouchardat's *albuminose* appears to agree partly with syntonin. It is obtained by treating blood-fibrin, egg- or serum-albumin, casein, or glutin with water containing $\frac{1}{2000}$th of hydrochloric acid, which, when fibrin is employed, leaves *epidermose* undissolved. The solution is lævorotatory, scarcely reddens litmus, becomes turbid when heated, and is precipitated by hydrochloric or nitric acid, the precipitate redissolving in a large excess of acid. It is precipitated by tannic acid, mercuric chloride, and ferrocyanide of potassium. This albuminose is regarded by Bouchardat as a ready-formed constituent of the substances from which it is derived (Bouchardat, *Compt. rend.* 14, 962; *Ann. Pharm.* 43, 120). According to Mulder & Baumhauer (*Ann. Pharm.* 47, 321) it contains, after precipitation with carbonate of ammonia and exhaustion with alcohol, 52·92 p. c. C., 6·81 H., and

15·88 N.; according to Verdeil, it contains 1·52 p. c. of sulphur (*Ann. Pharm.* 58, 317). According to Mulder, it is protein binoxide.

Preparation. 1. Very finely-chopped flesh is freed from soluble constituents by exhausting it with water and pressing; and the white tasteless residue is treated with water containing 0·1 p. c. of hydrochloric acid. The flesh is thereby dissolved to a thickish liquid rendered turbid by fat, which is filtered and precipitated by neutralising it with ammonia (Liebig). — 2. Fibrin or coagulated egg-albumin is dissolved in fuming hydrochloric acid; the filtrate is precipitated with water; and the precipitate is collected, pressed, dissolved in water, and again precipitated by careful addition of soda (Hoppe-Seyler).

Properties. Syntonin forms a moist, coherent, somewhat elastic white mass (Lehmann); when freshly precipitated, gelatinous flocks (Hoppe-Seyler). Rotates a ray of polarised light to the left; $[\alpha]\,\delta = 72^\circ$ in faintly acid or faintly alkaline solution; 84·8° after heating to 100° without access of air (Hoppe-Seyler).

Dried at 120° (Strecker).

	Fowl.	Ox.	Sheep.
C	54·46	53·67	
N	15·84		16·26
H	7·28	7·27	
S	1·21		
Ash	1·40		1·07

Walther (*Dissert.* Leipsic, 1851) found 1·6 p. c. of sulphur. —Bödeker (*Ann. Pharm.* 111, 195) gives the formula $C^{144}N^{18}H^{112}SO^{42}$.

Syntonin is insoluble in *water.* — When syntonin is boiled for 80 hours with frequently renewed water, with access of air, or when it is heated to 108° with water for eight hours, a yellow not swollen residue remains undissolved, and the colourless acid solution contains bodies precipitable by tannic acid, one of which, precipitable also by acids and soluble in excess of acid, is Meissner's *parapeptone;* the other body, not precipitable by acids is his *syntonin-peptone.* Besides these, lactic acid and creatinine, recognisable by the microscope, are produced (Meissner, *Zeitschr. für ration. Medicin* (3) 10, 18).

Syntonin dissolves easily in *hydrochloric acid* of 0·1 per cent. (Liebig). The solution is effected with the more difficulty the longer the syntonin is washed or kept moist, even though putrefaction is prevented by means of cold (Kühne). The solution is rendered opalescent by excess of hydrochloric acid (Lehmann). It does not coagulate on boiling; but when syntonin is boiled with water, it becomes insoluble, or soluble with difficulty, in hydrochloric acid of 0·1 per cent. (Kühne). The slightly acid solution is almost without action on *peroxide of hydrogen* (Giannuzzi, *Virchow's Arch.* 34, 443).

Syntonin does not dissolve in an aqueous solution of *nitrate of potash* containing 6 per cent. of the salt, nor in solutions of *chloride of sodium,* dilute or concentrated; moreover, chloride of sodium and other salts throw down from its solution in hydrochloric acid, a curdy precipitate soluble in a large quantity of water (Liebig). Chloride of sodium, chloride of ammonium, sulphate of soda, sulphate of magnesia, and chloride of calcium render cold dilute solutions of syntonin turbid, and form with strong solutions a thick jelly, from which white flocks are deposited on boiling (Kühne).

Syntonin dissolved in hydrochloric acid coagulates, when the solution is neutralised, to a thick white jelly which dissolves easily in excess of *alkalis* (Liebig). — Moist syntonin is easily soluble in aqueous *ammonia.* The solution is not precipitated by carbonic acid, or by the addition of other acids to neutral or acid reaction; it is completely coagulated by heat when exactly neutralised, but incompletely when a slight excess of acid or alkali is present. The liquid coagulable by heat is also precipitable by water. An ammoniacal solution, strongly acidified with acetic acid, is completely precipitated by mixing it with an equal bulk of a solution of sodium chloride (Eichwald).

Syntonin dissolves in very dilute solutions of alkaline *carbonates* (Kühne); in moderately strong carbonate of potash it swells up to a jelly which dissolves only after considerable dilution (Lehmann).

The solution in aqueous carbonate of soda containing 1 p. c. of the salt does not coagulate on boiling (Kühne). The alkaline solution is precipitated by nitric acid (Lehmann), and by carbonic acid, even in presence of alkaline phosphates (Hoppe-Seyler; Eichwald). Sulphate of soda scarcely precipitates the solution in carbonate of soda, even on boiling; but chloride of sodium, chloride of ammonium mixed with sulphate of magnesia, and chloride of ammonium alone (which salts render the solution only slightly turbid in the cold) throw down solid white flocks on boiling (Kühne). Chloride of calcium and sulphate of magnesia precipitate the alkaline solution only on boiling, but after the solution has been heated to the boiling point, they precipitate it even in the cold (Lehmann).

The precipitate produced by neutralising aqueous hydrochlorate of syntonin dissolves in *lime-water* if it has not been boiled with water. The solution coagulates on boiling like diluted albumin (Liebig). A solution of syntonin in lime- or baryta-water froths strongly when boiled; on prolonged boiling the froth is deposited in the form of transparent flocks, without much syntonin being precipitated. The solution is precipitated by chloride of sodium at the boiling heat but not in the cold: sulphate of soda causes no precipitate even on boiling; chloride of ammonium produces a slight precipitate in both cases; sulphate of magnesia and chloride of calcium precipitate only the hot solution. These reactions are not altered by boiling the syntonin solution and then leaving it to cool (Kühne).

Syntonin forms with strong *acetic acid* a jelly which does not dissolve completely in water (Hoppe-Seyler).

Platinocyanide of potassium throws down from a solution of syntonin in hydrochloric acid a precipitate which, after washing with water till it is free from acid, sets in a coherent mass over the water-bath and turns brown on drying. The percentage of platinum in the substance varies with the time of washing; after drying at 100° to 110° it contains from 3·91 to 4·20 per cent. (Diakonow, *Tübing. medic.-chem. Untersuch*, 1867, 1, 228). Platinocyanide of potassium throws down from acetate of syntonin a transparent jelly which quickly coagulates in flocks, becomes dense when heated, dissolves easily in mineral acids and in excess of the precipitant, and after drying at 110° contains 5·54 per cent. of platinum (Schwarzenbach, *Ann. Pharm.* 144, 68).

Ferrocyanide of potassium throws down from acetate of syntonin a precipitate free from potash, 1580 parts of syntonin being precipitated by 211 parts of the ferrocyanide (or by 108 parts of hydroferrocyanic acid) (Bödeker, *Ann. Pharm.* 111, 195).

Osmazome. Obtained by Thénard by exhausting flesh with water, evaporating the extract, treating the residue with alcohol, and evaporating the alcoholic liquid. It was pointed out even by Berzelius (*Lehrb.* 3 Aufl. 9, 575) that osmazome is a mixture of many substances and the same thing as an alcoholic extract of flesh. See Thénard (*Traité*, 4 ed. 4, 643); Vauquelin (*Ann. Chim.* 81, 37, and 85, 5); Mitscherlich (*Pogg.* 40, 127).—The *pseudotoxin* of Brandes (*N. Tr.* 11, 2, 71) from belladonna, and the *fungus osmazome* of Biltz (*N. Tr.* 11, 2, 71) from *Lycoperdum cervinum* are mixtures similarly prepared.

Paraglobin.

PANUM. *Virch. Arch.* 3, 251; 4, 17, and 19.

DENIS. *Mémoire sur le sang*, Paris, 1859, 37 and 181.

AL. SCHMIDT. *Müller's Arch.* 1861, 545 and 675; 1862, 428 and 533.

E. BRÜCKE. *Wien. Acad. Ber.* 2 Abth. 55, 881; *Chem. Centr.* 1867, 999.

EICHWALD. *Petersb. medic. Zeitschr.* 15, 239; *Chem. Centr.* 1869, 561.

Serum casein (Panum); *Serin* [Denis); *Globulin or Fibrino-plastic substance* (Schmidt); *Paraglobulin* (Kühne); *Paraglobin* (Brücke). Paraglobin, precipitable by acids from blood-serum diluted with water, was observed by Scherer, Lehmann, Zimmermann (*Müller's Arch.* 1854, 377), and Guillot & Leblanc (*Compt. rend.* 31, 520, and 585) previous to Panum's investigation. It was distinguished from serum albumin and more minutely examined by Panum, who called it serum casein. According to Al. Schmidt, it forms fibrin by contact with a second body, the fibrinogenous substance; but this view appears to have been rendered untenable by the researches of Brücke and Eichwald. See Fibrin.

Paraglobin occurs in blood, not only in the serum (Panum), but also, and in especial abundance, in the red blood-corpuscles; also in the fluid of connective tissue, in the cornea, and in many other parts of the animal body (Schmidt). According to Eichwald, it occurs also in the pericardial fluid, in which, however, Schmidt found none, or very little. According to J. C. Lehmann (*Virchow's Arch.* 36, 125) it is present in albuminous urine.

The *serin* of Denis, which Hoppe-Seyler (*Handbuch.* 184) regards as serum albumin, seems rather to belong to this place. It remains in solution in plasma after the separation of plasmin by means of sodium chloride; in serum after the separation of fibrin; and in whey after the separation of casein by sulphate of magnesia.

Denis agitates serum with one-third of its volume of cold ether, so long as a coagulum continues to be deposited; evaporates the filtrate at 40° to 50°; and re-dissolves the residue in the original volume of water. From this solution, diluted to ten times its volume, a few drops of very dilute hydrochloric or acetic acid precipitate the serin, which is to be separated from the supernatant liquid on the following day. Or, he saturates either plasma freed from plasmin with sulphate of soda at 40° to 50°, or serum freed from fibrin with sulphate of magnesia at 50°; collects the resulting precipitate at 50°; dissolves the soft white mass remaining on the filter in water; and precipitates the solution by largely diluting it, or better, by adding a few drops of very dilute hydrochloric acid. Serin is insoluble in water, but soluble in aqueous solution of sodium chloride; it is not converted into fibrin by agitation, neither is it coagulated by ether. It is coagulable by heat and by alcohol, and is quite insoluble in boiling weak spirit (Denis, *Mémoire sur le sang*, Paris, 1859, 37, and 181).

Preparation of Paraglobin. Horse blood is maintained in the fluid state by means of a freezing mixture, till the corpuscles have separated from the plasma; the latter is decanted and allowed to coagulate; the serum, free from corpuscles, thereby separated is diluted with 12 times its volume of very cold water; and a current of carbonic acid gas is passed through it. The solution becomes turbid at first, and after some hours deposits flocks, which are collected, dissolved in water, with addition of a few drops of very dilute soda-ley, and re-precipitated by carbonic acid (Schmidt).

Serum is rendered turbid, even by dilution with 10 to 20 parts of water, and on standing for 24 hours deposits paraglobin in the form of a white precipitate (Panum). When the solution is diluted with 100 parts of water, carbonic acid throws down not only paraglobin, but also a part of the syntonin, which remains undissolved on treating the precipitate with chloride of sodium (Eichwald).

Precipitated paraglobin forms microscopic, colourless, amorphous granules.—It dissolves to a very slight extent in *water*, and is deposited from the solution on standing for a few hours (Schmidt). When heated to 135° with water, for five hours, it acquires a yellowish-brown colour, and forms a yellow, scarcely acid solution, which is precipitated by nitric acid, neutral acetate of lead, sulphate of copper, corrosive sublimate, and tannic acid, but not by alcohol, and very slightly by acetic acid. Millon's mercury-solution and potassio-cupric tartrate show the presence of proteides, whereas peptones are absent (Werner: Schmidt, *Anal. Zeitschr.* 8, 132). Paraglobin, in neutral or slightly acid solution, decomposes *peroxide of hydrogen* in some cases, but not in all (Giannuzzi, *Virchow's Arch.* 34, 443).

Paraglobin dissolves very easily in *dilute acids* [slightly in water containing *carbonic acid* (Eichwald)], in caustic *alkalis*, and their *carbonates* and *phosphates*, and in aqueous solutions of *neutral salts*, especially *chloride of sodium*, *chloride of ammonium*, *sulphate of magnesia*, and the *chlorides of calcium* and *barium* (Panum). It forms with *potash-ley* a gelatinous albuminate, precisely as does egg-albumin (Brücke).

It is precipitated from its solution in *acetic* or *phosphoric acid* (see below) by *chloride of sodium*, *chloride of ammonium*, *acetate*, and *phosphate of soda*, *chloride of calcium*, and *sulphate of magnesia* (Panum).

On dissolving paraglobin in *alkaline water*, a feebly alkaline, somewhat opalescent liquid is obtained, which, when dried in a vacuum, leaves paraglobin, soluble with difficulty in water, but otherwise unaltered. The solution becomes covered with a pellicle of casein when evaporated; it is not precipitated by heat, and after being heated and allowed to cool, it exhibits no alteration of character, except that it is no longer fibrinoplastic. (According to Eichwald, however, acids throw down from a boiled neutral solution of paraglobin in alkalis, after cooling, a coagulum, which is insoluble in acids.) When whipped with a glass rod, the solution deposits part of the paraglobin, which is afterwards nearly insoluble in acids and alkalis (Schmidt).

Solutions of paraglobin containing *excess of acid* behave in the same manner as alkaline solutions when heated; but on heating paraglobin suspended in water, it collects together in large tough flocks, which dissolve in strong acetic acid or strong alkali on boiling only (Schmidt).

Carbonic and other *acids* precipitate faintly *alkaline* solutions of paraglobin the more completely the more dilute they are. The precipitate produced by *carbonic acid* dissolves gradually on passing *oxygen* or air through the solution; that produced by other dilute acids sometimes dissolves under the same circumstances, but only in presence of a slight excess of the acid, the precipitate reappearing when the solution is neutralised. Paraglobin is precipitated by strong *mineral acids*, but not by acetic acid (A. Schmidt). *Glacial acetic acid* forms with moist paraglobin a cloudy jelly, which gives with water a turbid solution, not rendered clear by boiling; weaker acetic forms therewith a transparent jelly (Brucke). A solution of paraglobin in acetic acid, when boiled for 10 or 15 minutes, forms Eichwald's *acidalbumin;* the solution is no longer coagulable by neutralisation, even when heated, but it is precipitated by chloride of sodium and acetic acid (Eichwald).

Paraglobin dissolves somewhat less freely in aqueous *monocarbonates of the alkalis* than in the caustic alkalis; still less freely in *bicarbonates of the alkalis*, and least of all in *neutral salts*. These last solutions are precipitated by dilution with water, more especially if a current of carbonic acid be passed into the solution at the same time, or acetic acid dropped into it (Schmidt). The solution in a half-saturated solution of sodium chloride is precipitated by acetic, but not by carbonic acid; the solution in faintly alkaline water is not precipitated by these or by other acids, after addition of chloride of sodium. Agitation with excess of chloride of sodium partially precipitates the paraglobin, without causing it to coagulate (Eichwald).

Solutions of paraglobin in *neutral salts* coagulate like solution of albumin when boiled (Eichwald). On heating such solutions, or slightly acid or alkaline solutions, to which neutral salts, even in small quantity only, have been added, precipitates insoluble in acids and alkalis are produced. On the other hand, solutions of paraglobin into which a current of oxygen is passed are not precipitated by heat, even in presence of acetate of soda (Schmidt).

A solution of paraglobin in *half saturated aqueous chloride of sodium* is not precipitated by carbonic acid. Alkaline (and acid) solutions of paraglobin are no longer precipitated by carbonic acid, after being mixed with an equal volume of saturated solution of sodium chloride (Eichwald).

A solution of paraglobin in *phosphoric acid* of 1 p. c. is not precipitated by heat, or by carbonic or acetic acid, but it gives with caustic soda an abundant precipitate soluble in excess of soda. Paraglobin dissolved in monophosphate of soda is not precipitated on neutralisation; nitric acid throws down from the solution a precipitate soluble in excess; the precipitate produced by heating the solution dissolves but incompletely in caustic soda. On dropping a faintly alkaline solution of paraglobin into excess of a dilute solution of monophosphate of soda, a turbidity is produced, which disappears on agitation at first, but afterwards becomes permanent while the solution is still acid, and does not disappear completely on adding paraglobin till the mixture becomes alkaline. Concentrated solution of monophosphate of soda is rendered permanently turbid only by a very large quantity of solution of paraglobin. Alkaline solutions of paraglobin mixed with chloride of sodium, or ordinary neutral phosphate of soda, are not affected by monophosphate of soda.

With *metallic salts* paraglobin behaves in the same manner as albumin, but the precipitate produced by sulphate of copper does not dissolve in excess of the precipitant (Schmidt). — Brücke found as follows:—A solution of fibrinoplasmin in chloride of sodium, or in caustic potash not in excess, gives with excess of sulphate of copper, a perfectly clear solution; but in presence of excess of potash, the solution is rendered turbid by hydrate of copper, the turbidity disappearing however on the addition of more potash or of glycerin.

Paraglobin is not precipitated from its solution in acetic acid by *ferrocyanide of potassium*. Paraglobin is insoluble in *alcohol* and *ether*, which liquids do not affect its chemical behaviour or its fibrinoplastic property (Schmidt). Paraglobin, which appears like birdlime when collected on a filter, contracts and becomes insoluble in cold acetic acid when alcohol is poured upon it (Panum). Alkaline or acid solutions are precipitated by alcohol (but not by ether) only when highly concentrated, or after addition of neutral salts (Schmidt).

Serum Albumin.

BERZELIUS. *Lehrb.* 3, Aufl. 9, 31.
MULDER. *Pogg.* 40, 277.
GOLDING BIRD. *Phil Mag.* [3] 1836, 109; 1837, 84; *J. pr. Chem.* 9, 32; 10, 308.
DUMAS & CAHOURS. *N. Ann. Chim. Phys.* 6, 404.
SCHERER. *Ann. Pharm.* 40, 1.
RÜLING. *Ann. Pharm.* 58, 310.
HOPPE-SEYLER. *Krit. Zeitschr.* 1864, 737; *Anal. Zeitschr.* 3, 424; *Kopp's Jahresber.* 1864, 614.

See further the memoirs referred to under Paraglobin.

Serumeiweiss. Blutalbumin. Formerly regarded as identical with egg albumin.

The albuminous substance thrown down in flocks on heating the blood-serum of vertebrate animals, and by similar treatment of lymph, chyle, serum, serous fluids, or muscle-serum, forms the serum albumin (blood albumin) of the older chemists. Panum's investigations revealed the presence of two albuminous bodies precipitable by heat under certain conditions, and in accordance therewith, serum casein (paraglobin) and serum albumin were regarded as distinct substances. Kühne supposes serum to contain also albuminate of soda, so that, according to him, three bodies must be distinguished, viz., paraglobin, precipitable by carbonic acid; albuminate, precipitable by acetic acid; and serum albumin, precipitable by heat. Brücke now again identifies paraglobin with serum albumin, and regards serum as containing only one albuminous substance, but distinguishes between *native* and *modified* albumin; whereas Eichwald's researches seem to show that serum contains not only paraglobin but also syntonin. The so-called soluble serum albumin would appear, therefore, to be a mixture of these two substances, or, more exactly, of paraglobin and syntonate of ammonia. Remembering, however, the experiments of Brücke and J. C. Lehmann on the influence exerted by even very small quantities of acetic acid on the properties of egg albumin, and also the fact of the presence of salts in serum, the pre-existence of syntonin in serum seems to require further proof (Kr.).

Serum albumin occurs, not only in the liquids mentioned above, but also in the fluids of many pathological cysts, in albuminous urine (which, however, according to J. C. Lehmann, contains paraglobin), abundantly in colostrum, and in small quantity only in milk.

The presence of albumin in milk is affirmed by Quevenne (*N. J. Pharm.* 21, 91); Doyere (*Arch. phys. nat.* 22, 239); Girardin (*N. J. Pharm.* 23, 401; *J. pr. Chem.* 60, 124); Morin (*N. J Pharm.* 25, 423; *J. pr. Chem.* 62, 509); Bodeker & Struckmann (*Ann. Pharm.* 97, 150); Heynsius (*Schmidt's Jahrb. der ges Med.* 95, 115); Trommer (ibid. 103, 5). Hoppe-Seyler distinguishes albumin from casein in the manner which will be described under Casein. For Lieberkuhn's objections to the occurrence of albumin in milk, see *Pogg.* 86, 298).—Commaille (*Récueil des mémoires de méd. militaire* [3], 17, 145 and 249; *Chem. Centr.* 1867, 588) distinguishes this albumin as *lactalbumin.* It dissolves in dilute ammonia-water more freely than egg albumin, and much less freely than casein. The orange-yellow platinum-compound contains 8·27 p. c. of platinum (Commaille).

Preparation. According to the older methods, coagulated serum albumin is obtained either by boiling (more advantageously with addition of not too much acetic acid or of chloride of ammonium), or by precipitating with alcohol, and is purified by washing and boiling with alcohol and ether.

Soluble serum albumin cannot be obtained free from alkali, acids, or salts, either by precipitating with basic acetate of lead, washing, and decomposing the precipitate with carbonic acid (whereby a solution containing acetic acid is obtained) (Lehmann; Scherer), or by dialysis. On attempting to diffuse out the acid from a solution of serum albumin acidified with acetic acid, by leaving it for four weeks in a dialyser at 0°, it is found that long after nothing but mere traces of salts has passed through into the water, the solution has deposited large flocks, which on examination prove to be serum albumin free from ash, but insoluble in water. The remaining solution still contains salts amounting to 1 p. c. of the solid constituents; a portion of the serum albumin remains unaltered, whilst a small portion is converted by the acetic acid into syntonin or acid-albumin (Kühne, *Physiol. Chem.* 179).

The serum albumin of Hoppe-Seyler and Kühne is obtained as follows:—Blood-serum or the fluid of hydrocele is diluted with twenty times its volume of water, and acetic acid is cautiously dropped into the solution; or a prolonged current of carbonic acid is first passed into the solution, and the albuminate of soda remaining in solution is then decomposed by acetic acid. After standing for 24 hours, the liquid is filtered and concentrated to a small bulk at 40° (according to Kühne after first adding carbonate of soda to restore the original alkaline reaction); and the residue is freed from the greater part of the salts contained in it by dialysis.

Eichwald's method of analysis of serum, by which he endeavours to prove the non-existence of a soluble serum albumin differing from paraglobin, is as follows:—

1. When blood-serum, diluted with ten times its bulk of water, is treated with carbonic acid, a finely pulverulent white precipitate of *paraglobin* is thrown down, and may be obtained pure by draining it as completely as possible on a filter, and washing with water till the filtrate is not rendered turbid either by nitrate of silver or by ferrocyanide of potassium acidified with acetic acid.

2. On cautiously adding to the liquid filtered from paraglobin, very

dilute acetic acid to distinctly acid reaction, loose brown flocks are deposited, increasing in quantity with the addition of acid up to that degree of acidity at which the fluid coagulates so completely on boiling, that the filtrate is not precipitated either by nitrate of silver or by ferrocyanide of potassium acidified with acetic acid. These flocks are *syntonin.*

3. The liquid filtered from both the above precipitates still contains a large quantity of coagulable substance, which is deposited in the form of a dirty-white precipitate, when the liquid is again largely diluted and allowed to stand for a day or two; it is almost completely precipitated on diluting the liquid to 400 or 500 times the bulk of the original serum, and adding rather more acid than is stated above. This precipitate is also *syntonin.*

4. The liquid thus treated at the proper degree of acidity, is now free from all but traces of coagulable substance, but contains *albumin-peptone*, which may be obtained by precipitating the remaining syntonin completely at the boiling heat, concentrating the filtrate, and precipitating the residue with absolute alcohol.

5. Inasmuch as blood evolves ammonia when warmed till it coagulates, and even at ordinary temperatures, and a solution of syntonin in ammonia likewise coagulates on boiling and is not precipitated by neutralisation with acids, it seems probable that the syntonin in the blood is present as syntonate of ammonia. The coagulation of a solution of serum-albumin would in that case depend upon the deposition of syntonin from the ammonia-compound, owing to loss of ammonia.

6. Further, when serum, freed from paraglobin and diluted with ten times its volume of water, is acidified with so much acetic acid that it no longer coagulates on boiling, but is completely precipitable by ferrocyanide of potassium, and is then mixed with an equal bulk of a saturated solution of chloride of sodium, syntonin is precipitated.

7. When serum, diluted with ten times its bulk of water and of the proper degree of acidity, is shaken up with mercury or collodion, a precipitate is produced, from which solution of sodium chloride takes up paraglobin, whilst carbonate of soda takes up syntonin (Eichwald).

Properties. Serum albumin is a pale-yellow, brittle, translucent mass, turning moist in the air.—It exerts a left-handed action on polarised light, $[\alpha]\,\delta = 56^\circ$: acetic and hydrochloric acids increase the rotatory power; potash-solution increases it to − 86° (Hoppe-Seyler).

	Mulder.	Scherer. *dried at* 100°.	Bence Jones.	Dumas & Cahours. *dried at* 140°.	Baumhauer. *dried at* 120°.
C	54·09	54·50	54·80	53·54	54·4
N	15·65	15·68	16·31	15·82	15·8
H	7·10	7·03	7·19	7·08	7·0
S	0·667				1·5
Ash		1·27	2·81	2·63	0·37

	Weidenbusch.		Rüling.	
	a.	*b.*	*dried at* 100°,	*dried at* 140°.
C	52·57	53·18	50·81	53·11
N	16 57	15·75		
H	7·29	7·03	7·09	7·01
S	1·59	1·56	1·38	
Ash	0 20	0·19	1·3	

Mulder's serum albumin from human blood contained 0·33 p. c. of phosphorus. Scherer analysed albumin from blood; Bence Jones (*Ann. Pharm.* 40, 67), albumin prepared from calf's brain. Dumas and Cahours analysed albumin from the serum of sheep's blood, and also from ox, calf, and human blood, with almost identical results.

Baumhauer (*Scheik. Onderzoek.* 4, 322; *J. pr. Chem.* 45, 120; *Kopp's Jahresber.* 1847 and 1848, 841) and Weidenbusch (*Ann. Pharm.* 61, 370; *Kopp's Jahresber.* 1847 and 1848, 840) prepared the albumin from flesh. The former chemist coagulates a cold aqueous extract of chopped fish-flesh at 50°, exhausts the coagulum with boiling water, alcohol, and ether, and dries at 120°. As thus prepared from soles, it contains 1·0 p. c. of ash, 1·03 sulphur, and 0·72 phosphorus; from cod-fish, 0·5 p. c. of ash, 1·31 sulphur, and no phosphorus. The albumin employed for analysis was dissolved in boiling acetic acid, precipitated by incomplete neutralisation with ammonia, and washed with boiling water, alcohol, and ether. Weidenbusch throws down the albumin from the cold watery extract by heat, and exhausts it with alcohol and ether; *a* is albumin from pike, *b* from poultry.

Many of the following observations on serum albumin are supplemented by the corresponding observations on egg albumin.

When blood-serum, obtained in the solid state by the spontaneous evaporation of the water, is triturated and washed with cold *water*, it is resolved into an insoluble portion, the ash of which is not alkaline, and a solution which yields on evaporation pellicles of casein, leaving an alkaline ash when incinerated (Scherer, *Ann. Pharm.* 40, 1).

Aqueous serum albumin *coagulates* at 72° or 73° in the form of flocks or a dense mass, the solution previously becoming turbid above 60° (Hoppe-Seyler). The temperature at which serum coagulates rises with the degree of dilution; a solution of the serum of ox-blood in 5 volumes of water no longer coagulates when boiled. Carbonic acid reduces the temperature of coagulation to a greater degree as the solution into which it is passed is more dilute, producing at the same time a flocculent deposit (Schmidt, *Muller's Arch.* 1862, 442). The addition of very weak phosphoric or acetic acid, or of chloride of sodium or other neutral salts, lowers the temperature at which coagulation takes place; a very small quantity of carbonate of soda raises it (Hoppe-Seyler).

Serum albumin is not rendered insoluble by *agitation*, like egg albumin; at least the turbidity thereby produced does not possess the fibrous character of egg-albumin which has become solid by agitation, or by passing into it a current of carbonic acid (Melsens, *Instit.* 1857, 201; *Kopp's Jahresber.* 1857, 531).

When serum albumin, dried at 100° and exhausted with ether, alcohol, and water, is *boiled with water* under a pressure of three atmospheres, a turbid solution is formed, which behaves like Mulder's protein trioxide (Hoppe-Seyler, *Virch. Arch.* 5, 171). Coagulated serum albumin, when heated to 150° with water in a tube for five hours, yields a very feebly alkaline solution, the filtrate from which is not precipitated by alcohol, but gives precipitates with dilute sulphuric acid, acetic acid, neutral acetate of lead, mercuric chloride, and sulphate of copper, and is distinctly coloured by Millon's mercury solution (p. 262). Solution of serum albumin prepared by Wurtz's method, when heated to 150° for 18 hours, yielded a neutral, nearly colourless solution; on opening the tube, a gas smelling of garlic escaped. The solution contained traces of ammonia-salts, but neither albumin nor peptone; it was not precipitated by alcohol, but gave precipitates with nitric and acetic acids, that produced by the latter being soluble in excess (W. Schmid, *Anal. Zeitschr.* 8, 130).

When serum-albumin free from fat is submitted to *electrolysis,* it yields at the positive pole, a curdy or cloudy mass which does not adhere to the pole; at the negative pole it remains transparent. The liquid at the positive pole acquires an acid reaction and smells of chlorine; that at the negative pole contains albuminate of soda. Serum-albuminates of the alkalis speedily coagulate at the positive pole; acid solutions sometimes coagulate at the negative (Golding Bird). The serum of rabbit's blood deposits coagulated serum albumin at the positive pole, only when the free alkali contained in it is first exactly neutralised (v. Wittich, *J. pr. Chem.* 73, 25). See also egg albumin, p. 286.

Serum albumin acted upon with *bichromate of potash*, or with *oxide of manganese* and *dilute sulphuric acid*, yields the same products as are obtained from casein (Guckelberger, *Ann. Pharm.* 64, 39).

Serum albumin precipitated by alcohol and washed, dissolves in a large quantity of water into which *carbonic acid* is passed, forming therewith a somewhat turbid solution, which behaves like diluted blood-serum when heated, also in its reactions with nitric acid, mercuric chloride, ferrocyanide of potassium, acetic acid, and tincture of galls. The serum albumin precipitated by carbonic acid from albuminate of soda and washed, behaves in a similar manner (Golding Bird).—*Phosphoric acid* does not precipitate serum albumin, and otherwise acts like acetic acid.

Coagulated serum albumin dissolves to a very slight extent in dilute *sulphuric acid* when digested therewith, but is converted into a sulphuric acid compound, which swells up and dissolves on washing, forming a solution precipitable by acids and alkalis (Berzelius).

Excess of strong *hydrochloric acid* throws down from solution of serum albumin a flocculent precipitate, which afterwards redissolves; water throws down from the solution hydrochlorate of syntonin, whilst a peptone remains in solution (Hoppe-Seyler). A solution of blood-serum in water containing from $\frac{1}{2000}$th to $\frac{1}{500}$th of hydrochloric acid exhibits the reactions of Bouchardat's albuminose (p. 268) (Bouchardat, *Ann. Pharm.* 43, 124).—Large quantities of *nitric acid* precipitate serum albumin; the concentrated acid dissolves it easily. The serum albumin of the urine is not completely precipitated even by a large quantity of nitric acid, but is converted thereby, or by heat, into xanthoproteic acid (Mehu, *Arch. génér de médecine*, 13, 257; *Chem. Centr.* 1869, 236).

Coagulated albumin turns soft and transparent in *acetic acid*, and on warming therewith, is converted into a tremulous jelly, which dissolves in water and is precipitated from the solution by alkalis (excess of which redissolves the precipitate), and by mineral acids and ferrocyanide of potassium. The acetic solution, when evaporated, leaves first a jelly, then a dry transparent mass, which reddens litmus and dissolves completely in warm water only after addition of acetic acid (Berzelius). Aqueous serum albumin is not precipitated by acetic acid.

Aqueous serum albumin, saturated with *nitrate of potash*, or with other *neutral salts*, is precipitated by *phosphoric* and *acetic acids* (Melsens). *Lactic*, *oxalic*, and *tartaric acids* behave in the same way; the filtrate is not precipitated either by boiling, or by the addition of nitric acid or ferrocyanide of potassium.—The precipitate produced by acids in saline solutions is Panum's acid-albumin. See p. 261.

Caustic ammonia acts but slowly on solutions of serum albumin, ultimately decreasing the molecular rotatory power of the solution; the resulting albuminous substance is precipitated on neutralisation (Hoppe-Seyler).—Solutions of *potash* and *soda* do not precipitate aqueous serum albumin, but convert it into albuminate, increasing the rotatory power, even when only small quantities of alkali are employed. By the prolonged action of the alkali, the rotatory power is again reduced (Hoppe-Seyler). In other respects also serum albumin exhibits the same behaviour towards alkalis as egg albumin.

Coagulated serum albumin swells up to a transparent jelly in aqueous *potash*, and then dissolves completely, forming a greenish-yellow solution (Berzelius) The solution is precipitated by acids with evolution of hydrosulphuric acid (Scheele); when it is digested with freshly precipitated hydrate of bismuth for 6 or 8 hours, at a nearly boiling heat, a quantity of sulphide of bismuth is formed, containing sulphur amounting to from 0 76 to 1·19 p. c. of the serum albumin (Fleitmann, *Ann. Pharm.* 66, 380).

Baumhauer dissolved coagulated albumin, obtained from fish, in dilute potash solution; heated the solution to 90° for some time, and passed through it a current of air; precipitated the filtrate with acetic acid; and boiled the precipitate with water, alcohol, and ether. He thus obtained a product containing 0 5 p. c. of ash, 54·7 C., 14·6 N., 7·0 H., and 1·1 S.—Protein prepared by precipitating serum albumin with alcohol, dissolving the precipitate in potash, and re-precipitating with acetic acid, contained, after drying at 140°, 1·2 p. c. of ash, 34·38 p. c. C., 15·92 N., and 7·14 H. (Dumas & Cahours, *N. Ann. Chim. Phys.* 6, 420).

A solution of serum albumin, to which a little caustic potash has been added, does not coagulate when boiled, but then forms on its surface a pellicle of casein containing 55·03 p. c. C., 15·63 N., 7·72 H. (Scherer, *Ann. Pharm.* 40, 1).

When blood-serum is mixed with solution of soda to alkaline reaction and heated, it is converted into a solid, transparent, scarcely alkaline jelly, which, on addition of water and further heating, yields a clear, somewhat slimy solution of albuminate of soda. This solution is not coagulated by alcohol or by heat, but is precipitated by acids, chlorine-water, alum, neutral acetate of lead, sesquichloride of iron, mercuric chloride, sulphate of copper, ferrocyanide of potassium, acetic acid, and tincture of galls. Carbonic acid passed into the solution, produces a precipitate which redissolves completely on continuing the current of gas; the solution now possesses the properties of an ordinary solution of serum albumin, and is precipitated by boiling; also by nitric acid, alum, mercuric chloride, and tincture of galls, but not by dilute acids or sesquichloride of iron (Golding Bird).

Fresh blood-serum, when boiled with an equal bulk of a cold saturated solution of *carbonate of soda*, evolves much carbonic acid; but the whole of the carbonic acid is not expelled from carbonate of soda, even by a large quantity of serum albumin. When carbonate of potash is employed, instead of carbonate of soda, no carbonic acid is evolved (Golding Bird).

Solutions in *carbonate* and *bicarbonate of soda* of serum albumin, precipitated by alcohol and washed, are precipitated by boiling also by nitric acid, alum, and mercuric chloride; acetic acid produces a precipitate soluble in excess of the acid (Golding Bird).

Serum albumin *mixed with aqueous alkalis*, is precipitated by *neutral salts*, and, on the other hand, aqueous alkalis precipitate solutions of serum albumin to which neutral salts have been added. With *chloride of sodium* the precipitate is thrown down even in the cold; with *sulphate of soda* only on heating. When the action of the alkali has been but slight, the precipitates thus thrown down dissolve in water; but when the action has been more intense, the precipitates are insoluble in water and aqueous alkalis, and soluble under certain conditions only in acids (Virchow). When serum albumin precipitated by boiling is dissolved in very dilute potash, and dry chloride of sodium is added, the solution is rendered cloudy at 35°, and deposits dense flocks at 45°. Sal-ammoniac, instead of chloride of sodium, causes at 50° a turbidity, and at 75° a deposition of dense flocks, which dissolve in a large quantity of water on heating, and are reprecipitated by sal-ammoniac (Panum, *Virchow's Arch.* 4, 445). On adding dry chloride of sodium to the serum of horse's blood, filtering from the resulting curdy precipitate and from excess of the chloride, and dropping strong soda-solution into the filtrate, a white precipitate is formed, settling in the form of a yellowish translucent jelly. This body does not dissolve in water on washing, but gives up thereto a substance precipitable by nitric acid and chloride of sodium. It swells up in acetic acid, but dissolves only in a large quantity of the boiling acid; and is insoluble in excess of solution of soda (Virchow, *Ann. Pharm.* 91, 344). This deposit is albuminate of soda, which dissolves in water after it has been washed free from alkali (Eichwald, *Würzburger. medic. Wochenschr.* 5, 356).

Blood-serum behaves like egg albumin towards *sesquichloride of iron*, *corrosive sublimate*, and *sulphate of copper;* the precipitate produced by the last salt contains 1·14 p. c. CuO. (F. Rose). — The serum of human blood, when neutralised with acetic acid, gives with *nitrate of silver* a precipitate containing 16·3 p. c. AgO. (Mulder, *Pogg.* 40, 277).

Serum albumin acidified with acetic acid behaves like egg albumin towards *platinocyanide of potassium* (Schwarzenbach, *Ann. Pharm.* 111, 195). According to Diakanow (*Tübing. medic. Untersuch.* 1867, 1, 232) precipitation takes place only after the conversion of the albumin into syntonin by the acid.

Serum albumin is precipitated from its aqueous solution by *alcohol*, albumin free from alkali and poor in salts being thereby thrown down; while another portion remains in solution as albuminate of soda. The precipitate dissolves slightly in pure water and easily in water containing salts (Lehmann, *Physiol. Chemie*, 1, 313). The precipitate redissolves in water at first, but in the course of a few minutes it is resolved into albuminate and coagulated albumin; by the prolonged action of alcohol, the latter alone appears to be formed (Hoppe-Seyler). Serum albumin containing alkali dissolves in hot alcohol, the solution on cooling depositing flocks which dissolve easily in water and in boiling alcohol (Scherer). — Serum albumin is not precipitated by agitation with *ether* (Hoppe-Seyler). — *Carbolic acid*, more especially when mixed with nitric acid, precipitates serum albumin (Mehu, *Chem. Centr.* 1869, 236). — Solution of serum albumin containing 5 p. c. produces with *pyrogallic acid* a precipitate soluble with difficulty in water, but easily soluble in excess of albumin and in aqueous carbonate of soda (G. Jüdell, *Tübinger medic. Unters.* 1, 423).

Scherer's *paralbumin* (*Handbuch*, viii, 235) and *metalbumin* (*ibid.*) are bodies related on the one hand to serum albumin and on the other to albumin-peptone. They occur chiefly in colloid sacs and render the fluid obtained therefrom slimy and ropy. *Paralbumin* is not thrown down as a solid coagulum by heating its solutions, but either does not coagulate at all, or converts the liquid containing it into a thick whitish mass, which forms an opalescent liquid with water. It is also less easily coagulable by alcohol, after addition of acetic acid, than albumin, and the precipitate thereby formed, after prolonged washing with alcohol, redissolves in water at 35° or 40°. Mineral acids throw from its solutions precipitates easily soluble in excess of moderately dilute acids. — *Metalbumin* is even less easily coagulable by alcohol or by heat than paralbumin, but is precipitable by metallic salts and by tannic acid. It is not precipitated by mineral acids, but on mixing it with excess of acid, the mixture is converted into a semi-fluid jelly. By ferrocyanide of potassium it is merely rendered cloudy, without being precipitated. On these bodies, see Scherer (*Würzburg. medic. Verhandl.* 2, 214 and 278; *Ann. Pharm.* 82, 135; *Kopp's Jahresber.* 1851, 579): Eichwold (*Würzburg. medic. Zeitschr.* 5, 336). On paralbumin, see also Haerlin (*Chem. Centr.* 1862, 884; *Kopp's Jahresber.* 1862, 552): Bökecher (*Virchow's Arch.* 6, 620); Plósz (*Hoppe-Seyler's Med.-chem. Unters.* 1871, 517).

Egg Albumin.

SCHEELE. *Opusc.* 2, 104. — THÉNARD. *Ann. Chim.* 67, 320; *Gilb.* 31, 106; HATSCHETT. *Phil. Trans.* 1799; *Scher. J.* 6, 305. — BOSTOCK. *N. Gehl.* 4, 547; *Schw.* 29, 397.

BERZELIUS. *Schw.* 10, 142; *Pogg.* 9, 631; 10, 247.

LINK. *Schw.* 14, 294. — BRANDE. *Gilb.* 64, 354. — CHEVREUL. *Ann. Chim. Phys.* 19, 46; *Gilb.* 70, 379.

Prévost & Dumas. *Ann. Chim. Phys.* 23, 52.
J. Vogel. *Ann. Pharm.* 30, 20; *Berzel. Jahresber.* 20, 549.
F. Rose. *Pogg.* 28, 132.
Mulder. *Pogg.* 40, 271. — *J. pr. Chem.* 44, 489.
Ad. Wurtz. *Compt. rend.* 18, 700; *J. pr. Chem.* 32, 503; *Berzel. Jahresber.* 25, 874.
Melsens. *N. Ann. Chim. Phys.* 33, 170; *J. pr. Chem.* 54, 383; *Kopp's Jahresber.* 1851, 576. — *Belg. Acad. Bull.* 24, No. 2; *Instit.* 1857, 201; *Kopp's Jahresber.* 1857, 531.
Lieberkühn. *Pogg.* 86, 117 and 298; *J. pr. Chem.* 57, 352; *Kopp's Jahresber.* 1851, 692.
Theile. *Jenaer medic. Zeitschr.* 3, 147; *N. Br. Arch.* 138, 19; *Kopp's Jahresber.* 1867, 774.

White of egg. Albumin of birds' eggs. To be distinguished from serum albumin and vegetable albumin.

Forms the chief part of the organic substance of the white of birds' eggs, which is rendered viscid by the presence of the membranes permeating it, and contains, besides albumin, small quantities of albuminate and paraglobin, traces of fats or soaps, grape-sugar, and a quantity of ash amounting to about 3 p. c. of the solid constituents. — On crystals of an albuminous body from the white of hens' eggs, see Ar. Boettcher (*Virchow's Arch.* 32, 525; *Anal Zeitschr.* 4, 262); on *Oonin*, a body separated from white of egg by freezing, see Couerbe (*J. Pharm.* 15, 497; *Ann. Chim. Phys.* 41, 323).

On differences between the whites of fowls' and pigeons' eggs, see Jahn (*N. Br. Arch.* 37, 259; *Berzel. Jahresber* 25, 875).

On the formation of albumin or coagulable albuminous bodies from casein, according to Sullivan, see Casein.

According to Danilewski's preliminary communication (*Krit. Zeitschr. f. Chem.* [2], iv, 12, 41) there exists in the white of hens' eggs an optically inactive albumin containing 2 p. c. of sulphur, by the splitting up of which albuminous substances are obtained, having a left-handed rotatory action on polarised light. In these bodies the sulphur is said to be combined in part indirectly and in part directly with oxygen; but an albumin may be obtained in which the sulphur exists only in the latter state. Albumin containing 2 p. c. of sulphur, in being resolved into *a*, *b*, *c* albumin containing 1·3, 1·1, 0·9 p. c. of sulphur, yields at the same time fatty acids, neurine, and cholic acid as decomposition-products.

Preparation. The coagulated albumin employed for the analyses given below was prepared either by boiling filtered white of egg and washing the coagulum with water and alcohol (Mulder), or by precipitating filtered white of egg with alcohol, and washing with alcohol, water, and ether (Lassaigne, *Ann. Chim. Phys.* 20, 98; Dumas & Cahours, *N. Ann. Chim. Phys.* 6, 407; Theile). Ruling adds a few drops of hydrochloric acid before precipitating with alcohol.

Wurtz precipitates diluted and filtered white of egg with basic acetate of lead, not in excess; suspends the washed precipitate in water, and passes carbonic acid through the liquid; filters; precipitates traces of lead from the filtrate by a few drops of aqueous hydrosulphuric acid; and heats the clear brown liquid to 60°, whereupon the sulphide of lead goes down with the first flocks of albumin. He then filters again and evaporates the filtrate at 50°. According to Scherer (*Würzburg medic. Zeitschr.* 5, 318) and Kühne (*Physiol. Chemie*, 178) the albumin thus prepared contains acetic acid, and is precipitable by ammonia, and has therefore already undergone alteration.

Graham (*Ann. Pharm.* 121, 61; *Kopp's Jahresber.* 1861, 80) purifies egg albumin by submitting to dialysis the white of hens' eggs mixed with acetic acid; after 3 or 4 days, albumin free from ash remains on the dialyser. It then possesses a slight acid reaction, coagulates milk heated with it, and still contains the sulphur pertaining to its constitution. Kühne was unable in this manner to get rid of the salts from serum albumin without at the same time rendering it insoluble. This albumin doubtless contains acetic acid.

Von Wittich (*J. pr. Chem.* 73, 18; *Kopp's Jahresber.* 1858, 541) dilutes white of egg with water, with addition of a little carbonate of soda; precipitates the albumin as acidalbumin by hydrochloric acid; collects the precipitate, and washes it with water containing hydrochloric acid; suspends it in water at 50°; precipitates the milky liquid with carbonate of ammonia; and washes the precipitate with water, cold alcohol, and ether. The egg albumin thus obtained is insoluble in water and neutral salts, also in bicarbonate and neutral phosphate of soda, but dissolves in aqueous neutral carbonate of soda and monophosphates of the alkalis, and combines with acids to form compounds which are soluble in pure water, and are precipitated on neutralising their solutions with alkalis. It is, therefore, at any rate, altered albumin, probably having been converted into syntonin (Kr.).

Hoppe-Seyler (*Anal. Zeitschr.* 3, 425; *Handb.* 186) cuts up white of egg with scissors; squeezes it through linen; filters without access of air to prevent incipient browning; dilutes with a large quantity of water; and precipitates a few flocks or fibres of an albuminous substance soluble in hydrochloric acid by careful addition of acetic acid, or by a current of carbonic acid. The filtrate may be freed from salts by dialysis or by Wurtz's method.

According to these experiments, and those given under serum albumin, albumin in a soluble state has not been obtained free from ash, and from acid or alkali, and hence the view put forward by Scherer, Denis (*Mémoire sur le sang*, 187), and others, viz., that egg albumin and animal albuminous substances generally are in themselves insoluble in water, and become soluble only after combination with salts or alkalis, appears to be well-founded. This view is further supported by the following statement of Kühne:—When white of hens' eggs is largely diluted with water, it deposits nearly the whole of the albumin held in solution by salts, whilst albuminate of potash and globulin remain in solution. After precipitating these also by careful addition of acetic acid, the filtrate becomes slightly turbid only on boiling, owing to the small quantity of albumin remaining dissolved in the very dilute saline liquid (Kühne, *Physiol. Chemie.* 553). Denis cites the following experiment: On diluting filtered white of egg with from 5 to 20 parts of water, and adding a few drops of very weak hydrochloric or acetic acid, a turbidity is gradually produced, which dissolves in water containing chloride of sodium [or nitrate of potash (Scherer)], and is reprecipitated from this solution by more water. Eichwald (*Wurzburg. medic. Zeitschr.* 5, 318) also describes albumin as insoluble in water, and soluble only with the aid of alkalis and their salts.

Properties. Dried albumin forms a hard, brittle, white, or yellowish translucent mass of conchoïdal fracture, and without taste or smell.—Aqueous egg albumin rotates a ray of polarised light to the left; $[\alpha]\,\delta = 35{\cdot}5^\circ$: hydrochloric acid increases the angle of rotation to $37{\cdot}7^\circ$;

strong caustic potash at first increases it to 47°, or with coagulated albumin to 58·5°, and afterwards reduces it (Hoppe-Seyler, *Anal. Zeitschr.* 3, 425).—According to Hruschauer and Wurtz, it has a faint acid reaction, even after coagulation, but does not give up acid to water.

	Gay-Lussac & Thénard.	Mulder. *dried at* 125°.	Scherer. *at* 100°.	Dumas & Cahours. *at* 140°.
C	52·88	53 73	53·78	53·37
N	15·71	15 52	15·92	15·77
H	7·54	7·02	7·07	7·10
O				
S		1·6		
Ash		2·03	2·0	1·13

	Rüling.		Wurtz.		Theile.
	dried at 100°.	*at* 140.	*a.*	*b.*	*dried at* 130°.
C	52·81	54·33	52·79	52·92	53·98
N			15·55	15·65	14·24
H	7·26	7·13	7·13	7·15	7·51
O					22·34
S	1·77				1 93
Ash	1·68				2·3

Wurtz analysed soluble (a) and coagulated (b) egg albumin. After exhaustion with ether, it contained 52·82 p. c. of carbon.—Theile's numbers are calculated from the analysis of albumin dried over chloride of calcium, allowance being made for water expelled at 130°.

Mulder's albumin contained also 0·4 p. c. of phosphorus. Verdeil (*Ann. Pharm.* 58, 317) found 2·109, Schwarzenbach (*Ann. Pharm.* 133, 185) 1·85 to 22 p. c. of sulphur.—The ash is deducted in all cases.—Formulæ of albumin: $C^{180}N^{22}H^{139}S^{2}O^{60}$ (Mulder); $C^{216}N^{27}H^{169}S^{3}O^{68}$ as empirical formula (Liebig); $C^{72}N^{9}H^{56}SO^{22}$ for albuminic acid (Lieberkuhn); $C^{148}N^{17}H^{224}S^{2}O^{46}$ (Theile).

Egg albumin dried over chloride of calcium contains 45·85 to 46·58 p. c. C., 7·62 to 7·96 H., 12·14 N., 1·63 S., after deducting 2·3 p. c. of ash. It loses 12·76 p. c. of water at 100° to 130°, turning slightly brown even at 100°. At 165° it suffers no further loss, and at still higher temperatures empyreumatic ammoniacal decomposition-products are formed.

Uncoagulated albumin, after evaporation to dryness, forms with 4 parts of cold *water* a mass resembling fresh albumin, and with more water a slimy solution. Egg albumin evaporated below 50° likewise dissolves in water.—When a solution of the white of hens' eggs, free from membrane, is allowed to drop from a filter into water, each drop becomes covered with a fine insoluble pellicle, and falls to the bottom undissolved (Kühne, *Untersuch. uber das Protoplasma*, 20).

Albumin may be rendered insoluble by *motion*, and then assumes the appearance of fibres or membranes. This formation of membranes takes place also with albumin purified by Wurtz's method. It occurs when, in filtering a solution of albumin, the drops are made to fall from a height; when dry or moist air, hydrogen, or carbonic acid, is passed through the solution, even under a layer of oil; when the solution is shaken for 24 hours in a closed flask, or when it is shaken in a vacuum. On evaporating *in vacuo* a solution of albumin saturated with chloride of sodium, there remains a residue soluble in water, from which the insoluble membranes separate on passing carbonic acid through the solution, or on agitation (Melsens). See Harting's objections (*Schmidt's Jahrb.* 75, 148; *Kopp's Jahresber.* 1852, 691), and Melsens' reply (*Instit.* 1857, 201; *Kopp's Jahresber.* 1857, 531). Denis also obtained a large quantity of fibrillæ, insoluble in water and chloride of sodium, by prolonged agitation of albumin. To this place belong, apparently, Smee's observations noticed under Fibrin.

The albumin of birds' eggs *coagulates* when heated to 63° to 75°, that is, it becomes converted into a white, slightly translucent, solid, somewhat elastic mass, drying up to a yellow horny substance, which when immersed in water assumes the appearance of freshly coagulated albumin, without dissolving.

The white of hens' eggs remains clear at 60°, becomes slightly turbid at 63°, begins to solidify at 65°, and becomes completely solid at 70° to 75° (Dumas and Prévost). Perfectly neutral solution of the white of hens' eggs (free from albuminate of soda and globulin) becomes turbid at 57°; forms a white pulp at 60°, and deposits large flocks at 62° to 64° (Lehmann, *Virchow's Arch.* 36, 115). The white of ducks' eggs begins to coagulate at 63° (Chevreul). Fresh albumin, mixed with $\frac{1}{2}$ part of water, coagulates completely when heated; with 1 part of water it remains slightly fluid; with 10 parts no coagulum is produced, but a milky turbidity, which is perceptible even with 1000 parts of water (Bostock). — A solution of Wurtz's egg albumin becomes turbid at 59·5°, forms flocks at 63°, and solidifies at a somewhat higher temperature. — On the behaviour of albumin diluted with water at 38°, see Arnold (*Schmidt's Jahrb.* 103, 1).

The coagulation takes place also in vessels exhausted of air, without evolution of gas or change of volume or temperature. Fresh-laid eggs, when covered at once with oil, do not coagulate completely, but only become milky. — It is attended with the formation of hydrosulphuric acid. Metallic silver is blackened by albumin when hot, but not when cold; coagulated albumin blackens acetate of lead, and also lead-paper held over it, after addition of acids (Gobley, *N. J. Pharm.* 18, 347). The coagulation is accompanied by elimination of alkali [ammonia (Eichwald, *Chem. Centr.* 1869, 568)], which combines with another portion of albumin to form albuminate (Scherer). Egg albumin dried at a low temperature is not coagulated, even at 100° [or above 100° (Brücke)] in the dry state (Al. Schmidt, *Muller's Arch.* 1862, 447).

Albumin in the pure state, or mixed with chloride of sodium, after being immersed, in a closed tube, in a mixture of solid carbonic acid and ether, recovers its fluidity on exposure to the air (Melsens).

Commaille distinguishes boiled albumin as *pexin*. It dissolves with difficulty in slightly acidulated water. When its solution in caustic soda is precipitated by hydrochloric acid, and the precipitate is dissolved in water, a solution is formed, from which bichloride of platinum throws down a dark orange-yellow precipitate containing 7·80 p. c. of platinum (Commaille).

When albumin mixed with an equal volume of water and strained is evaporated in the sun, or exposed in an open vessel for six days, it no longer coagulates on boiling, but at a certain degree of concentration solidifies to a translucent jelly which is soluble in water. The addition of very dilute acetic, formic, tartaric, or citric acid, by which the solution is not precipitated, restores the property of coagulation (Monnier, *Par. Soc. Bull.* 11, 470). According to Monnier a peculiar modification of albumin is thus produced.

Hard-boiled white of egg heated to 150° with *water* for 2 or 3 hours, dissolves therein, forming a solution which is precipitated by acids (Wöhler, *Ann. Pharm.* 41, 238). When it is heated to near 200° with water in a copper digester, the walls of the vessel become covered with a film of sulphide of copper, and the albumin dissolves, with exception of a portion which remains unaltered. The solution contains a little free acid, and substances partly soluble and partly insoluble in alcohol. — When coagulated albumin is boiled for some time in water, it swells up strongly, softens, decomposes, and gives up animal matters to the water (Gmelin).

Mulder (*Ann. Pharm.* 47, 314) found that when white of hens' eggs was boiled in a Papin's digester for 150 hours, there remained a portion insoluble in water and alcohol, containing 54·34 p. c. C., 15·33 N., and 7·16 H., unaltered albumin according to Mulder. The aqueous solution, when evaporated to dryness, left a residue which, after exhaustion with alcohol, dissolved in water and gave a precipitate with neutral acetate of lead, and a further precipitate with the neutral acetate and ammonia. Both precipitates were decomposed by hydrosulphuric acid. The substance thus obtained is Mulder's protein trioxide containing 50·75 to 51·36 p. c. C., 6·69 H., 15·01 N. It is neutral soluble in cold water, precipitable by dilute mineral acids, chlorine, and metallic salts, but not by acetic acid, ferrocyanide of potassium, chloride of ammonium, or chloride of barium.

Undiluted white of hens' eggs, when submitted to *electrolysis*, deposits a dense white layer of coagulated albumin at the positive pole, and if the experiment be continued long enough, the negative pole becomes covered with a clear jelly of albuminate of soda, which last does not appear with diluted albumin. Solutions of alkaline albuminates likewise deposit the albumin in films at the positive pole; acid solutions of albumin deposit it more slowly at the negative pole, in the form of a diffused cloud, whilst alkali or acid is set free at the opposite pole. If the solution contains free acid, free alkali, or monocarbonate or bicarbonate of alkali, the deposit of albumin does not take place, or takes place very slowly; but if the solution contains neutral salts, such as chloride of sodium, phosphate of soda, sulphate of soda, sulphate or nitrate of potash, the deposit at the positive pole is much more abundant (v. Wittich). — The following are older statements:—Albumin alone or diluted with water is completely coagulated at the negative pole (Arnim, *Gilb.* 8, 259; Marx, *Schweig.* 54, 209). With a strong current, a rapid deposit takes place at the negative, and a slower deposit at the positive pole; with a very weak current, there is a deposit at the positive pole, whilst an alkaline solution of albumin is formed at the negative (Brande, *Gilb.* 64, 354). With a weak current, C. G. Gmelin (*Gilb.* 64, 347) observed coagulated albumin at the positive pole only, never at the negative; a strong current caused coagulation at both poles, which Gmelin attributes to the heat evolved. Lassaigne (*Ann. Chim. Phys.* 20, 97) precipitated albumin with alcohol, washed the precipitate with weak spirit to free it from chlorides, and submitted its aqueous solution to electrolysis, which did not cause coagulation excepting after addition of chloride of sodium, and then only at the positive pole. According to Morin (*Par. Soc. Bull.* 1861, 104) this result is due to the low conducting power of the liquid. Morin's other statements agree with those of v. Wittich; for those of Golding Bird, see *Serum albumin.* According to Smee (*Proceedings*

Roy. Soc. 12, 399 and 505; 13, 350; *Kopp's Jahresber.* 1863, 617; 1864, 614) fibrin is formed by the electrolysis of egg or serum albumin.

Moist uncoagulated albumin rapidly *putrefies*, with evolution of hydrosulphuric acid; coagulated albumin does not putrefy, even under water. — When albumin is dissolved in 40 to 50 parts of water and exposed to the air for a few weeks, at the temperature of 25°, the following products of putrefaction are formed: *a*. Products which pass over on distilling the liquid with milk of lime. These are ammonia and a body of penetrating odour, part of which goes over in crystalline laminæ when the ammoniacal liquid is distilled with phosphoric acid, while another portion may be extracted from the distillate by ether. It is very volatile and assumes a rose-red to brown-red colour with dilute sulphuric acid, forming oily drops. — *b*. Volatile acids obtained by distilling the residue containing lime with a slight excess of sulphuric acid. — *c*. When the residual liquid from the last operation is mixed with neutral acetate of lead, there is thrown down with the sulphate of lead, a plaster-like precipitate, from which hydrosulphuric acid separates brown acid oily drops. — *d*. When the liquid remaining after separating the plaster-like lead-salt is freed from lead by hydrosulphuric acid, it yields on evaporation a viscid syrup which is resolved by alcohol into leucine and a soluble portion. The latter is free from sulphur, has an acid reaction, forms with lead-oxide a salt soluble in alcohol, and when boiled with sulphuric acid yields tyrosine and a brown colouring matter (Bopp).

Albumin submitted to *dry distillation* yields carbonic acid, hydrosulphuric acid and combustible gases, water, hydrocyanic acid, carbonate of ammonia, and empyreumatic oils, whilst a nitrogenous coke and ash remain behind (Hatschett). — In the open *fire* dried albumin puffs up, emits an odour of burning feathers, blackens, and burns, leaving charcoal.

When *ozonised air* is passed through aqueous albumin, the solution becomes turbid and reddish, or by transmitted light greenish-yellow, and deposits tough, greyish-white, fibrous masses, which afterwards redissolve. The clear acid liquid ultimately remaining is not precipitated by heat, or by acids or metallic salts, with the exception of basic acetate of lead, but is rendered turbid by alcohol. It contains neither sugar nor urea, and a very small quantity of any solid substance in proportion to the albumin employed. Its constituents are for the most part uncrystallisable and acid, and resemble peptones; alcohol takes up from them some acid crystals, probably benzoic acid (Gorup-Besanez, *Ann. Pharm.* 110, 96). When a little alkali is added to the albumin, the phenomena observed are the same up to the deposition of the fibrous masses; after some days' action of the ozone, the liquid contains albuminates, which subsequently disappear (Gorup-Besanez, *Ann. Pharm.* 125, 221). — Albumin freed from paraglobin and precipitated with alcohol, decomposes *peroxide of hydrogen* in neutral or slightly acid solution, less rapidly than ordinary albumin, and not at all after boiling (Giannuzzi, *Virch. Arch.* 34, 443; *Krit. Zeitschr.* 1865, 749).

Albumin is decomposed by *bromine* and water in sunshine (Blomstrand, *Ann. Pharm.* 123, 248). — Albumin dissolved in water is coagulated by *chlorine* (Thomson), forming Mulder's proteinchlorous acid (p. 265); the filtrate contains a little humin, besides salts (Mulder).

Albumin reduces *chromic acid* and decolorises *manganic acid* (Hünefeld, *J. pr. Chem.* 7, 40).

Permanganate of potash, in dilute solution, acting upon albumin at the temperature of 50° to 55°, with gradual addition of sulphuric acid not in excess, is slowly decolorised and decomposes the albumin, so that when 3 to 3½ parts of the permanganate are employed to 1 part of albumin, the solution is no longer rendered turbid by heating it with acetic acid. The products formed are (besides carbonic acid, ammonia, and other substances) benzoic acid and a yellow syrup insoluble in alcohol, but no urea (Städeler, *J. pr. Chem.* 72, 251; *Chem. Centr.* 1858, 90). Previously to this, Béchamp (*N. Ann. Chim. Phys.* 48, 348; *Ann. Pharm.* 100, 247; *Kopp's Jahresber.* 1856, 696) thought he had obtained urea by the action of permanganate of potash on albumin, and he maintains the opinion in later memoirs (*N. Ann. Chim. Phys.* 57, 291; *Kopp's Jahresber.* 1859, 181; *Compt. rend.* 70, 866; *Zeitschr f. Chem.* [2], 7, 347). After addition of sulphuric acid to albumin till the alkaline reaction is not quite destroyed, permanganate of potash forms, it is said, first an acid, then urea, and lastly, when all organic matter has disappeared, sulphate of ammonia. From the products first formed a substance differing from albumin, and insoluble in water, may be isolated. Two or more acids, characterised by their action on polarised light and by their different degrees of solubility in alcohol and ether-alcohol, are said to be formed.

Subbotin (*Chem. Centr.* 1865, 593; *Krit. Zeitschr.* 8, 693) observed as follows:—When egg albumin is oxidised with permanganate of potash at 50° to 60° (for which 32 to 35 grammes of permanganate to 83 grammes of white of egg, corresponding to 10 grammes of albumin, are necessary) and the product is distilled, there passes over an acid aqueous liquid smelling of bitter almond oil and valerianic aldehyde. The residue does not contain urea; on neutralising it with sulphuric or carbonic acid, evaporating, and treating the residue with boiling alcohol, sulphate of potash is left undissolved, nearly corresponding in quantity to the sulphur of the albumin, when carbonic acid is employed for neutralisation. The alcoholic solution contains benzoic acid amounting to 1·55 p. c. of the albumin employed, and leaves on evaporation a syrup from which three or four substances may be separated by successive treatment with ether, cold and hot absolute alcohol, and water. These bodies are: *a.* An orange-yellow oil soluble in ether. *b* and *c.* Nitrogenous potash-salts, which are extracted by cold and boiling alcohol, and, after drying at 100°, rapidly deliquesce to viscid masses. *d.* A yellowish-brown viscid mass easily soluble in water, hard and brittle at 100°; it contains nitrogen and is precipitable by bichloride of platinum.

According to Wanklyn, Chapman, & Smith (*Chem. Soc. J.*, 20, 448) albumin gives up one-third of its nitrogen as ammonia when boiled with a caustic alkali, and the remaining two-thirds on subsequent boiling with permanganate of potash.

Most *mineral acids* throw down from aqueous albumin precipitates containing the acids in combination with albumin in the insoluble state. Phosphoric acid, acetic acid, and other vegetable acids, do not precipitate solutions of albumin, but form acid albuminates, which are precipitated on neutralising the solutions with alkalis. — Employed in excess, the mineral acids form decomposition-products, especially when strong and hot.

The turbid fresh solution of egg albumin in water is not precipitated by addition of small quantities of sulphuric, hydrochloric, or nitric acid, but on the contrary becomes clearer and is afterwards not precipitated, or is rendered only slightly turbid, by boiling (Günsberg, *Wien. Acad. Ber.* 45, 643; *Chem. Centr.* 1863, 460).

The precipitates produced by very dilute acids dissolve in a large quantity of water; those produced by acids less dilute do not re-dissolve in excess of the acids (Eichwald, *Würzb. medic. Zeitschr.* 5, 318).

a. Carbonic acid does not precipitate aqueous solutions of egg albumin, but from undiluted white of egg it throws down fibres, flocks, and pellicles, which are not readily dissolved either by acids or by alkalis (Hoppe-Seyler, *Handbuch*, 187). Al. Schmidt regards the precipitate as paraglobin (*Müller's Arch.* 1862, 447).

b. Freshly ignited *phosphoric acid* dissolved in water precipitates aqueous albumin abundantly, but loses this property in time (Engelhart, *Kastn. Arch.* 6, 340; Berzelius, *Pogg.* 9, 631). Albumin is precipitated by metaphosphoric acid mixed with acetic acid, but not by salts of pyrophosphoric or orthophosphoric acid.

Phosphoric acid in excess does not precipitate albumin, but the solution mixed with it is precipitated by neutralisation with alkaline carbonates (Berzelius). A mixture of monophosphate of soda (or acid sulphate of soda) and egg albumin yields no acid albuminate, even on long standing and warming (J. C. Lehmann, *Virchow's Arch* 36, 125).

c. Strong solution of *boracic acid* throws down from undiluted white of egg, white flocks soluble in chloride of sodium; from an aqueous solution it throws down part of the albumin as paraglobin (Brücke). The precipitate is insoluble in excess of a dilute solution of boracic acid, and only partially soluble in a strong solution. The turbid liquid thus formed is precipitated by a small quantity of ferrocyanide of potassium, the precipitate dissolving in excess of the precipitant, and in chloride of sodium; also by a small quantity of chloride of sodium, whereas a larger quantity of this salt forms a clear solution which deposits dense flocks on boiling; also by a small quantity of potash, the precipitate dissolving in a larger quantity of potash while the liquid is still acid, and in aqueous chloride of sodium and ferrocyanide of potassium (Brücke, *Wien. Acad. Ber.* 2 Abth. 55, 881; *Chem. Centr.* 1867, 1005).

d. Egg albumin forms with *sulphuric acid* a soluble and an insoluble compound (Berzelius, *Lehrbuch,* 3 Aufl. 9, 33 and 37).

α. Soluble Albumin-sulphuric acid.—On dropping dilute sulphuric acid into white of egg mixed with a little water till the liquid is distinctly acid, the cellular tissue is deposited, and the perfectly transparent filtrate leaves, on evaporation in a vacuum, a translucent yellow mass, which when immersed in water, swells up, softens, and dissolves, with the exception of some coagulated albumin-sulphuric acid. The colourless, acid, but insipid solution becomes opalescent at 57°, opaque at 61°, and coagulates completely at 65°, from separation of coagulated albumin-sulphuric acid, with simultaneous liberation of sulphuric acid. Sulphuric, hydrochloric, and acetic acids, and alcohol, throw down from albumin-sulphuric acid, precipitates which do not dissolve on diluting the liquids with water.

β. *Insoluble Albumin-sulphuric Acid.* — Moderately dilute sulphuric acid precipitates albumin (less completely than nitric acid) in white flocks, which become hard and yellow on drying, and do not dissolve in water when washed therewith, but give up to it nearly the whole of the sulphuric acid (Berzelius). These flocks, when freed from sulphuric acid by washing for six weeks, and afterwards washed with alcohol and ether, have the composition of albumin (54·52 p. c. C., 15·83 N., 7·60 H.), and redden litmus-paper when laid upon it, but do not give up free acid to water (Hruschauer, *Ann. Pharm.* 46, 348). See also Berzelius (*Jahresber.* 24, 657).

Dry albumin swells up in oil of vitriol to a jelly, which shrinks in water and leaves Mulder's protein-sulphuric acid (Mulder). Coagulated albumin dissolves almost entirely in cold oil of vitriol, forming a brownish-yellow liquid precipitable by water (Link). Hot oil of vitriol carbonises albumin, without forming artificial tannin (Hatschett); it produces a large quantity of ammonia (Heintz, *Pogg.* 68, 393). Boiling dilute sulphuric acid converts albumin into a purple mass, but does not dissolve it (Mulder): by prolonged boiling it forms the same products of decomposition as hydrochloric acid (Bopp), and among them aspartic acid (Kreussler, *J. pr Chem.* 107, 240).

¶ According to O. Loew (*J. pr. Chem.* [2] iii, 180; *Chem. Soc. J.* [2], ix, 409) the compound formed when albumin is immersed in strong sulphuric acid, is *albumin-sulphuric acid* $C^{72}N^{9}H^{54}SO^{22},SO^{3}$: it is a white, tasteless and scentless powder, insoluble in dilute acids, soluble in dilute alkalis.

When dried albumin is treated with a mixture of strong nitric acid and *sulphuric acid* in the cold, and the mixture, after standing for several hours, is thrown into cold water, a precipitate is formed consisting of *trinitro-albumin-sulphuric acid*, $C^{72}N^{9}H^{51}(NO^{4})^{3}SO^{22},SO^{3}$. This acid is a bitter yellow powder, insoluble in water, alcohol, and dilute acids, but soluble in dilute alkalis, forming a red solution, from which it may be reprecipitated unchanged. By the action of sulphide of ammonium it is converted into *triamido-albumin-sulphuric acid* $C^{72}N^{9}H^{51}(NH^{2})^{3}SO^{22},SO^{3}$, a brownish-yellow powder, having a faint taste, soluble in dilute alkalis. Strong alkalis decompose it, especially on warming, with evolution of ammonia. Nitric acid dissolves it with evolution of red fumes. It is insoluble in dilute acids, but when freshly precipitated dissolves readily in concentrated acids. It does not react like the proteides with Millon's test (Loew) ¶.

When the whites of thirty hen's eggs, coagulated by means of *absolute alcohol*, are agitated with a mixture of 600 or 700 c.c. of absolute alcohol and an equal volume of *oil of vitriol*, the albumin dissolves in the course of ten minutes to a violet, afterwards brown liquid, which, after boiling for some time, is no longer precipitable by ammonia. On neutralising the solution, an odour of allyl or oil of mustard is evolved: the solution contains ammonia and deliquescent salts, having the composition of tyrosine-sulphates (W. Knop, *Chem. Centr.* 1868, 141).

Albumin is decomposed by boiling with aqueous *iodic acid* (Millon, *Compt. rend.* 19, 272).

ε. Egg albumin may be strongly acidified with *hydrochloric acid* without coagulating: a larger quantity of the acid produces a whitish turbidity, and then throws down flocks of a compound of hydrochloric acid with an albuminous substance. These flocks dissolve with difficulty in water, are nearly insoluble in dilute hydrochloric acid and saline solutions, and dissolve but slowly and incompletely in fuming hydrochloric acid (Hoppe-Seyler, *Handbuch*, 187). The precipitate contains, on the average, 3·9 p. c. of hydrochloric acid (Mulder). — When white of egg is allowed to drop from a filter into hydrochloric acid of 0·1 p. c., it coagulates like muscle-plasma, and afterwards dissolves in the liquid. The solution at first coagulates on boiling, but ceases to do so after 24 hours, and then exhibits all the reactions of syntonin [or of Bouchardat's albuminose (p. 268) (Bouchardat)] (Kühne, *Untersuch.* 20) See also Arnold (Schmidt's *Jahrb.* 103, 1). — On prolonged contact with hydrochloric acid, albumin assumes a red or blue colour, and forms a blue solution. Strong hydrochloric acid at the boiling heat dissolves coagulated albumin with black-brown colour (Link). The coloration is caused by exposure to air: when air is excluded, a straw-yellow solution is obtained, which, on exposure to air, assumes a blue colour, changing to purple, and ultimately to black, the solution then containing ammonia and humic acid (Mulder). When albumin is boiled for 6 or 8 hours with strong hydrochloric acid, and the liquid is evaporated, there remains a black-brown syrup containing leucine, tyrosine, and leucimide. After these bodies have crystallised out, the syrup is sweet and not susceptible of fermentation: after boiling with potash, it evolves hydrosulphuric acid on addition of acetic acid, forms a violet solution with alkaline solutions of cupric oxide, and dissolves lime, baryta, oxide of lead, and oxide of copper (Bopp). — Egg albumin takes up 11·5 p. c. of hydrochloric acid gas at 14° (Mulder).

When albumin precipitated by alcohol is heated to 80° with a mixture of one volume of *fuming hydrochloric acid* and five volumes of water for two hours, in a current of carbonic acid, a portion dissolves, while a smaller portion is converted into a translucent jelly which, after the solution is poured off, dissolves in water, and is again precipitated by hydrochloric acid. In this operation, hydrosulphuric acid and small quantities of volatile organic acids are evolved. After washing with water and drying, the jelly is triturable to a greyish-white powder, which swells up to a tremulous jelly in water, and dissolves on heating. Its aqueous solution is precipitated by alum, neutral acetate of lead, ferric sulphate, stannic chloride, mercuric chloride, and ferricyanide of potassium in the cold, and by ferric chloride on warming, but not by ferrocyanide of potassium. The jelly contains (after deducting 0·74 p. c. of ash) 51·77 to 52·02 p. c. C., 7·42 H., 12·89 N., 1·42 S., and therefore less nitrogen than chondrin, which it otherwise resembles in its reactions. — The solution filtered from the jelly contains chloride of ammonium and a nitrogenous acid free from sulphur, the amorphous magnesia-salt of which contains 41·20 p. c. C., 6·08 H., 11·34 N., 29·56 O., and 11·76 MgO., corresponding to the formula $C^{52}N^{6}H^{45}O^{22},4MgO$. No leucine or tyrosine is formed (L. Mayer & Rochleder, *Wien. Acad. Ber.* 24, 38; 30, 166; *Chem. Centr.* 1858, 63 and 573; *Kopp's Jahresber.* 1857, 533; 1858, 540).

Coagulated albumin dissolves in dilute hydrochloric acid on addition of yeast, though more slowly than fibrin. See Fibrin (Dumas, *Berzel. Jahresber.* 25, 872).

f. Nitric acid throws down from aqueous solutions of albumin a white precipitate, which turns pasty and dissolves on washing, and is re-precipitated in yellow flocks by nitric acid in excess. The precipitate dissolves also in acetic acid, and, according to Thénard, in ammonia and potash, provided the nitric acid employed is not concentrated. The precipitation is the more complete the stronger the acid and the solution of albumin, and it is accelerated by warming. Very weak nitric acid turns yellow after some weeks, and converts the albumin into a yellow mass, which, after washing with cold water, dissolves in hot water and gelatinises on cooling (Hatschett).—Excess of nitric acid, on warming, dissolves albumin coagulated by heat, or by nitric acid itself, with evolution of nitric oxide, nitrogen, carbonic acid, and hydrocyanic acid. The solution is a dark-yellow liquid, which is precipitated by water, gives a dark-brown precipitate with ammonia, and after prolonged action of the nitric acid, contains oxalic acid (Hatschett). The solution contains an ammonia-salt, afterwards oxalic and saccharic acids, and leaves xanthoproteic acid when evaporated (Mulder). Liquid white of egg coagulates when mixed with half its volume of fuming nitric acid, becoming hot and yellow. On further heating, the mixture froths violently, evolves a large quantity of nitric oxide, and yields a clear solution, from which a small quantity of an amorphous substance is deposited on cooling (Muhlhäuser). See also the decomposition of proteides by nitric acid (pp. 257, 258).

g. Albumin dried at 130° is insoluble in *acetic acid* (Mulder).—Aqueous egg-albumin is not precipitated by excess of acetic acid, either in the cold or on boiling, but the acid solution is precipitated by neutralisation with carbonates of the alkalis (Berzelius). In this reaction, acetic albuminate is formed, which remains in solution in presence of small quantities of acetic acid, but gelatinises in presence of larger quantities (J. C. Lehmann).

When albumin is treated with *strong acetic acid*, it swells up to a jelly, which dissolves on addition of water, especially when warmed. On evaporating the solution, acetic acid is volatilised, the liquid becoming covered with froth, and solidifying to a jelly, which leaves coagulated albumin when evaporated to dryness (Berzelius). Albumin dried in the sun, or evaporated to $\frac{1}{3}$rd its volume at 40°, coagulates when acetic acid is poured upon it, and, after washing away the acid, is then insoluble in water, but soluble in dilute acetic acid. Albumin purified by Wurtz's method behaves in the same way. The insoluble albumin thus formed contains, at 130°, 53·08 p. c. C., 7·19 H., and 1·706 S. (Lieberkühn, *Virch. Arch.* 5, 162).

The first effect of the action of acetic acid is to render the albumin precipitable by acids. On precipitating with acetic acid a solution of albumin mixed with chloride of sodium, and filtering off the precipitate at once, a filtrate is obtained which again becomes turbid on standing. The first precipitate is soluble in water, and is not thrown down on neutralising the solution, provided that the acid has not acted too long (Brücke).

The formation of acetic albuminate takes place even in very dilute solutions; immediately in solutions which contain, after mixing, 1 p. c. of albumin (free from albuminate of soda and globulin) and 0·3 p. c. of acetic acid, and in more dilute solutions after standing for some time, or on heating to 40°. In such cases the solutions remain clear, so that the albuminate reveals itself only on neutralising them with weak soda. When the solutions contain, after mixing, 30 p. c. of acetic acid and 2 p. c. of albumin, a jelly is produced. A much larger quantity of acetic acid dissolves the jelly or prevents its formation, which, however, is then brought about by heating the mixture to a temperature varying between 40° and 68°, the lower the greater the quantity of acid present; or by mixing the solution with an equal volume of alcohol. When the proportion of acetic acid is below 1 or 1½ p. c. of the anhydrous acid to 1 p. c. of albumin, the solution coagulates at 73°, or when mixed with alcohol, to a white pulp, soluble in water. — The formation of acetic albuminate is attended with evolution of carbonic acid and separation of mucin-like flocks, and takes place also in vessels from which air is excluded.

The jellies liquefy on heating them to 92° to 97°, if they contain at least 8 p. c. of acetic acid to 1 p. c. of albumin, and more easily in presence of a larger proportion of acid; with less acid, turbid slimy masses are produced. On cooling they solidify unchanged. They dissolve easily in boiling water; but those jellies which contain little acid lose this solubility when heated to 75° or 85° without water, or when mixed with excess of absolute alcohol.

Gelatinous acetic albuminate, when evaporated in the air, leaves a residue, which is insoluble in water, slightly soluble in aqueous carbonate of soda, more easily in solution of caustic soda containing 0·5 per cent., and nearly insoluble in aqueous phosphate of soda and dilute acetic acid (Lehmann).

A solution of albumin highly concentrated at 40° gives with strong acetic acid, no jelly, but a curdy precipitate, insoluble in water (Lieberkühn, *Virchow's Arch.* 5, 163). This precipitate, when heated without washing, melts to a clear liquid, which solidifies again on cooling, and is insoluble in water both before and after melting. A clear, fusible jelly, soluble in hot water, is obtained only by dropping a solution of albumin into excess of strong acetic acid, with constant stirring; in this case it is obtained even with concentrated solutions of albumin (J. C. Lehmann, *Virch. Arch.* 36, 110).

Coagulated albumin forms a jelly, though with difficulty, on prolonged boiling with strong acetic acid. In certain proportions it swells up to a gelatinous mass, which does not melt when heated, and is incompletely soluble in boiling water (Lieberkühn). A jelly is not formed, or is formed only very incompletely, by solid albumin heated above 85°; but albumin precipitated from weak acid solutions at 63°, is at once converted into a jelly by acetic acid (Lehmann).

Albumin is coagulated by a very small quantity of *lactic acid* (Gay-Lussac & Pelouze).

An aqueous solution of white of egg, to which *chloride of sodium* or other *neutral salt* has been added, is precipitated by *phosphoric*, *acetic*, *lactic*, *oxalic*, and *tartaric acids*. The filtrate contains no albuminous substance, precipitable by heat or by nitric acid or ferrocyanide of potassium (Panum). See Acid albumin (p. 261)

Coagulated albumin dissolves in aqueous *ammonia*, and leaves on evaporation yellow transparent fragments, which swell up and dissolve in water, forming a solution that does not coagulate when boiled. The ammoniacal solution is coagulated by a small quantity of acetic acid, and by alcohol, the precipitate formed by acetic acid dissolving in excess (Payen & Henry). White of egg mixed with carbonate of ammonia, like that mixed with caustic ammonia, is precipitated by neutralisation (J. C. Lehmann, *Virchow's. Arch.* 36, 125).

When soluble albumin is mixed with aqueous *alkalis*, or when coagulated albumin is dissolved therein, albuminates are formed at first. On boiling the solution, or digesting it for some time with excess of alkali, sulphide of the alkali-metal and other decomposition-products are formed, and ultimately ammonia, leucine, and other substances; at no period of the action is Mulder's protein free from sulphur produced. See the articles Protein, Albuminic acid, Casein. Fused hydrate of potash forms leucine and tyrosine, with evolution of ammonia, hydrogen, and odorous gases (Bopp).

A solution of albumin in moderately strong potash-ley does not blacken acetate of lead, or evolve hydrosulphuric acid, which first makes its appearance on boiling with potash-ley the precipitate produced by acetic acid (Liebig, *Ann. Pharm.* 57, 131).

Potash-ley of sp. gr. 1·45, forms with boiled albumin, at 14° or 15°, only a small quantity of sulphide of potassium, acetate of lead being scarcely blackened thereby; but on boiling the solution, a large quantity of sulphide is produced. When the mixture is kept at the temperature of 50° for a quarter of an hour to three hours, sulphide of potassium is formed, to a less extent than on boiling, and the precipitate then thrown down by acetic acid contains sulphur. On further heating, the quantity of sulphide of potassium formed increases up to 102°, as the temperature is higher, the precipitate thrown down by acetic acid diminishing in the same proportion. All the substances produced below the boiling-heat yield sulphide of potassium, as do also those formed on boiling, at least when fused with hydrate of potash (Laskowski). According to Brücke, solid albuminate of potash (see *Albuminic acid*), previous to washing, evolves hydrosulphuric acid when treated with acids.

When a solution of egg albumin in a very small quantity of dilute potash-ley is heated as long as the sulphur-reaction continues to become more distinct, and the product is mixed with hydrate of bismuth or finely divided silver, till a test-portion boiled with potash and oxide of lead no longer yields sulphide.—then filtered, and precipitated with acetic acid, a white precipitate (*a*) is obtained, whilst the solution, when evaporated to a syrup and mixed with a large quantity of alcohol, deposits a second precipitate (*b*). — The precipitate *a*, after washing, dries up to a transparent, dark-yellow, easily friable mass, which floats on boiling water as if melted, and does not dissolve in absolute alcohol. — The precipitate *b* resembles *a*, but is easily soluble in water. Both are free from sulphur, or contain only very little. — Albumin dissolved in potash-ley evolves hydrosulphate of ammonia when boiled with chloride of ammonium, but the whole of the sulphur is not separated by boiling even for many hours (Laskowski, *Ann. Pharm.* 58, 158).

According to Mulder, when albumin is dissolved in potash-ley and the solution is exposed to the air, his protein is produced, the albumin losing phosphorus in the form of hypophosphite, whilst the sulphur is oxidised, and products soluble in water and alcohol are formed. Caustic potash in excess evolves ammonia on boiling, and produces carbonic acid, formic acid, leucine, protide, and erythroprotide. On neutralising the potash with sulphuric acid, evaporating the solution, and boiling the residue with alcohol, the boiling liquid deposits erythroprotide in brown oily drops, and on evaporating, crystals of leucine, formiate of potash, and protide are obtained. a. *Erythroprotide* is a reddish-brown, soft body, precipitable from its aqueous solution by salts of the metals. — b. *Protide* is isolated by dissolving the above products in water, adding neutral acetate of lead to the solution to remove erythroprotide, then precipitating with the basic acetate, and decomposing this precipitate with hydrosulphuric acid. It is an amorphous, straw-yellow body, not precipitable by mercuric chloride, nitrate of silver, or tannic acid. On this substance see Liebig (*Ann. Pharm.* 57, 129).

Fleitmann (*Ann. Pharm.* 61, 121) in endeavouring to prepare Mulder's protein free from sulphur, found as follows:—On digesting crude white of egg, or albumin purified by precipitation with alcohol, with an equal volume of 2 p. c. potash-solution at 60° to 90°, in a shallow basin exposed to the air, the jelly produced at first became fluid, and the sulphide of potassium formed in the course of a few hours disappeared again. After standing 14 days, and while the solution still evolved hydrosulphuric acid with acids, it was precipitated with acetic acid, the precipitate appearing only after the liquid had become strongly acid. This precipitate, which contained 1·42 p. c. of sulphur, was horny at 100°, and was not wetted by water, but dissolved in ammonia and in acetic acid either strong or weak. Another precipitate similarly prepared but with somewhat stronger potash-solution, to which hydrate of bismuth was added, contained, on the average, 53·95 p. c. C., 7·21 H., 16·09 N., and 1·41 S. (Fleitmann).

Theile (*Chem. Centr.* 1867, 385) found, on boiling albumin with ten times its weight of potash dissolved in alcohol for ten hours, at intervals of several days, that ammonia was given off, amounting to 4·46 p. c. of the albumin. In this case the albumin was in contact with the potash for three weeks altogether; when the distillation is continued without intermission, as long as ammonia is evolved, it amounts to 2·72 p. c. of the albumin. Baryta-water produces 3·07 p. c. of ammonia, and 4·5 p. c. of carbonic acid (Theile). Weak solution of carbonate of soda, boiled with diluted white of egg, eliminates at most $2\frac{1}{2}$ p. c. of the nitrogen in the form of ammonia (Wanklyn, *J. pr. Chem.* 103, 58). Distillation with potash-ley evolves $\frac{1}{3}$rd, and after addition of permanganate of potash, the whole of the nitrogen as ammonia (Wanklyn, Chapman, & Smith, *J. pr. Chem.* 102, 333). See also Campbell (*J. pr. Chem.* 102, 355), and *Kopp's Jahresber.* 1867, 828.

One part of vitellin albumin (obtained from yolk of egg by treating it with ether till it is decolorised, and washing the residue with absolute alcohol) when digested for three weeks with $1\frac{3}{4}$ parts of potash, and 3 parts of water at 5°, yields a clear dark-brown ammoniacal liquid, which, when freed from ammonia by boiling and neutralised with sulphuric acid, changes from brown to yellow and green, and evolves carbonic acid and a repulsive putrid odour. The solution, diluted with water, filtered, evaporated, and exhausted with alcohol, yields 70 p. c. of leucine and tyrosine, besides the following bodies:

a. Flocks, which are deposited on neutralising with sulphuric acid and diluting with water. They are grey, like the proteides, elastic at first, but hard and brittle after drying, and contain when dried at 120° (after deducting 3·92 p. c. of ash) 66·31 p. c. C., 6·17 N., 10·66 H., 0·72 S., and 16·14 O., and consist probably of an intermediate decomposition-product.

b. A reddish-brown extract, partially soluble in absolute alcohol, and completely in 90 p. c. alcohol. Its solution in absolute alcohol deposits crystals easily alterable in the air, and having, according to Theile, the formula $C^8NH^9O^7$.

c. A second reddish-brown extract, insoluble in absolute and in 90 p. c. alcohol. This body, the ash of which amounts to at least 24·25 p. c., likewise crystallises, and, according to Theile, is probably represented by the formula $C^8NH^9O^4$. For the properties of these bodies see Theile (*N. Br. Arch.* 118, 19, and 57).

White of egg mixed with *potash* is not rendered turbid by an aqueous solution of *chloride of sodium*, and becomes turbid only after some days when saturated with the powdered salt (Panum). Lieberkühn found albuminate of potash precipitable on addition of chloride of sodium and warming. The precipitation takes place either in the cold or only on warming, accordingly as the albumin is more or less diluted with water, but is determined more especially by the amount of potash and salt; the precipitate is in some cases soluble, in others insoluble, in water (Virchow). Thus white of egg diluted with twice its volume of water, and mixed with strong soda-ley, is precipitated in large flocks by chloride of sodium, whilst white of egg saturated with chloride of sodium, coagulates on addition of soda-ley [according to Eichwald (Wurzb. *medic. Zeitschr.* 5, 356) from separation of albuminate of soda, which dissolves in water after washing] or on boiling. When white of egg is saturated with sulphate of soda and filtered, the filtrate is precipitated by boiling, but not by addition of soda-ley. These precipitates are insoluble in water and in excess of soda-ley. When, on the other hand, white of egg diluted to 8 times its volume is mixed with very weak soda-ley, warmed for some time, and filtered, and a large quantity of dry sulphate of soda or a warm saturated solution of the salt is added, an abundance of large flocks is thrown down. These flocks diffuse themselves in water, and dissolve on warming, and are precipitated by the addition of soda-ley, but not by boiling (Virchow, *Ann. Pharm.* 91, 334). Eichwald (Würzb. *medic. Zeitschr.*) found white of egg, either pure or diluted, precipitable by agitation with crystals of chloride of sodium, the precipitate being perfectly soluble in water; when potash was added before the chloride of sodium, the precipitate, after washing, was less easily soluble in water the greater the quantity of potash employed, but always rapidly soluble in acetic acid.

Coagulated albumin prepared by Wurtz's method expels carbonic acid from *carbonates* and *bicarbonates of the alkalis* on heating (Wurtz). — *Borax* acts on albumin in the same way as free alkali (Brücke).

White of egg hardens with *lime:* coagulated albumin dissolves in lime-water (Scheele). A solution of the white of one egg in a pound of water does not precipitate *baryta- strontia-* or *lime-water*, or solution of *sulphate of lime* (Thomson).

Solutions of *alum* and *sulphate of alumina* throw down from aqueous albumin, white precipitates, which are soluble in excess of the precipitants and in albumin, and are free from sulphuric acid (F. Rose).

Albumin does not precipitate *arsenious acid*, or prevent the detection of it, but the precipitate thrown down by hydrosulphuric acid contains albumin (Simon, *Pogg.*40, 308; Kendall, *Pharm. J. Trans.* 9, 526; *Kopp's Jahresber.* 1850, 555). When a mixture of 1 part of arsenious acid with 100 parts of albumin is coagulated by heat, the arsenic remains in solution, or may be washed out of the coagulum (Edwards, *Pharm. J. Trans.* 9, 524; *Jahresber.* 1850, 555). See also Muspratt (*Chem. Soc. J.* 4, 178); Herapath (*Phil. Mag.* [4] 2, 345); *Jahresber.* 1851, 580. — Albumin is not precipitated by *tartar-emetic* (Simon).

Aqueous albumin gives a slight white precipitate with chloride of zinc (Bostock). It throws down from *sulphate of zinc* a white precipitate soluble in excess of albumin and in excess of sulphate of zinc; the precipitate contains 2·73 p. c. of oxide of zinc, but no sulphuric acid, and dissolves easily in aqueous ammonia, carbonate of soda, sulphate of copper, and acetic acid (F. Rose).

Albumin forms a hard mass with *oxide of lead* (Scheele). Aqueous albumin precipitates *neutral acetate of lead* copiously, the precipitate dissolving in excess of the acetate (Simon). It gives even with dilute *basic acetate of lead*, a precipitate, which, according to Mulder (*Pogg.* 40, 271), contains 12·31 p. c., but when the mixture is boiled 6·8 p. c., of oxide of lead. — Aqueous albumin precipitates *nitrate of bismuth*, and renders *bichloride of tin* slightly milky. *Protochloride of tin* does not cause turbidity in albumin (Simon), but forms ammonia on digestion therewith (Schenk & Chapman, *Chem. Centr.* 1868, 311). — Aqueous albumin gives a white precipitate with *ferrous sulphate.*

Sesquichloride of iron throws down from albumin a brownish-red precipitate, soluble in excess of the iron-salt. With concentrated solutions the mixture solidifies to a jelly. — The moist precipitate dissolves easily in aqueous sulphate of copper, acetic acid, potash, and carbonate of soda, forming solutions which are not affected by boiling. The precipitate contains, on the average, 2·84 p. c. of ferric oxide, but no chlorine (F. Rose).

Aqueous albumin precipitates *cuprous chloride* white; *cupric sulphate* and *nitrate* greenish-white (Bostock). It throws down from cupric sulphate a greenish precipitate, soluble in excess of albumin but not in excess of the copper-salt, and containing 1·60 to 1·69 p. c. of oxide of copper, but no sulphuric acid. The precipitate dissolves in a cold solution of carbonate of soda, easily in acetic acid, forming a solution which is not affected by boiling; in ammonia with deep blue, and in potash-ley with violet colour, the latter solution depositing oxide of copper on boiling, without being decolorised (F. Rose). The precipitates formed vary in composition according as the albumin or the cupric salt is in excess, the precipitate in the former case containing basic sulphate, in the latter case neutral sulphate of copper. Both precipitates are decomposed by prolonged washing with water, losing much sulphuric acid, a little oxide of copper, and organic substance (Mitscherlich).

a. On dropping cupric sulphate into excess of albumin, the precipitate formed at first redissolves on agitation, but becomes permanent with more cupric sulphate, and generally disappears but partially on addition of excess of the copper-salt. The pale-blue precipitate contains 2·8 p. c. of *cupric oxide* in the form of basic sulphate with 3 at. CuO. to 1 at. SO^3.

b. The bluish-green precipitate produced on dropping albumin into excess of cupric sulphate, redissolves at first, but on addition of more albumin, the cupric salt being still in excess, a permanent precipitate is formed containing 5 8 to 6·7 p. c. CuO,SO^3.

Both these compounds, after washing, are insoluble in albumin and in solution of cupric sulphate. They behave in a similar manner towards reagents, but their reactions differ according as they are treated in the moist washed state, or dry, or in solution.

The *moist washed precipitates* dissolve easily in sulphuric, hydrochloric, and nitric acids, forming solutions from which excess of the acid throws down white precipitates. They dissolve with green colour in acetic and oxalic acids, excess of which does not precipitate the solution. The solution in ammonia is of a fine blue, afterwards brown colour; that in potash-ley is a beautiful violet. The precipitates dissolve completely in aqueous iodide of potassium; partially in phosphate of soda, leaving a pale-green residue; and completely in ferrocyanide of potassium, with fine brownish-red colour. They are insoluble in alcohol and ether.

The *dried* precipitates, which are of a dark-green colour, dissolve partially in weak acetic acid, leaving a transparent jelly, and slowly in sulphuric acid.

The green *solution of the precipitates* in acetic acid behaves as follows:—Hydrosulphuric acid turns it brown, and throws down, from strong solutions only, a few brown flocks; hydrosulphate of ammonia throws down a yellowish-brown precipitate soluble in excess; iodide of potassium throws down a yellow, and ferrocyanide of potassium a reddish-brown precipitate. All these precipitates contain organic substance (C. G. Mitscherlich, *Pogg.* 40, 106).

The precipitate produced from cupric sulphate and albumin is a mixture of albuminate of copper and sulphate of albumin, the latter of which, together with a portion of the former, may be extracted by water, so that the residue then does not contain a larger quantity of sulphuric acid than of albumin (Mulder, *Berzel. Jahresber.* 18, 537.—*Pogg.* 14, 444). A solution of the precipitate in potash-ley is turned brown, but not precipitated by hydrosulphuric acid; it is precipitated by ferrocyanide of potassium only after addition of acids (Simon, *Pogg.* 40, 308).

When *hydrated oxide of copper* is mixed with albumin, and potash-ley is added, a fine violet solution is formed. The same result is produced by adding cupric sulphate to albuminate of potash (C. G. Mitscherlich). The latter solution deposits coagulated albumin on addition of acids, whilst copper-salt remains in solution (Monnier, *Analyt. Zeitschr.* 4, 237).—See also p. 262, and K. Graf (*Pharm. Viertelj.* 7, 117).

Mercurous nitrate throws down from albumin a white precipitate, which rapidly turns slate-grey, dissolves in potash-ley, forms calomel with hydrochloric acid, and mercurous acetate with acetic acid (Geoghegan, *Ann. Pharm.* 24, 36; Bostock).—*Mercurous chloride* is not affected by agitation with aqueous albumin (Lassaigne). In a mixture of calomel, chloride of sodium, and water, more mercury is recognisable after addition of albumin than before: the calomel assumes a grey colour, and contains metal, part of the mercury being dissolved as mercuric chloride or oxide (Voit).

On triturating moist *mercuric oxide* with albumin, a compound is obtained which behaves in the same way as the precipitate thrown down from albumin by mercuric chloride, but is not so white. The same compound is formed also with albumin and mercuric nitrate or acetate (Geoghegan). Moist mercuric oxide dissolves in albuminate of potash (Lassaigne). Mercuric sulphate and nitrate throw down from albumin precipitates containing 4·99 to 14·74 p. c. of mercuric oxide (Commaille).

Mercuric bromide produces with albumin a less copious precipitate than mercuric chloride of the same strength, and in dilute solution does not affect it (Lassaigne, *J. Chim. méd.* 12, 178).

Aqueous albumin precipitates *mercuric chloride* white, most completely in warm solutions, even when highly dilute: the precipitate dissolves in excess of albumin, but not in excess of the mercury-salt.

The precipitate is a compound of mercuric chloride with albumin (Lassaigne), but when washed for a day it loses the whole of its chlorine, and there remains a compound of mercuric oxide with albumin (Elsner).

a. The precipitate containing mercuric chloride is a white, tasteless, curdy mass, which turns yellowish, translucent, and horny on drying. In the moist state it dissolves rapidly in aqueous chloride of sodium, chloride of potassium, and chloride of calcium, and likewise in iodides and bromides of the alkali-metals, aqueous phosphoric, sulphurous, arsenious, oxalic, acetic, tartaric, and malic acids, but not in sulphuric, nitric, hydrochloric, or gallic acid. Its solutions in aqueous neutral salts deposit coagulated albumin containing a large quantity of mercuric chloride when heated: they give up mercuric chloride to ether. — The precipitate dissolves easily in aqueous ammonia, potash, and soda, and in lime-water, forming solutions which quickly become turbid from separation of metallic mercury (Lassaigne, *Ann. Chim. Phys.* 64, 90).

b. The precipitate obtained free from chlorine by prolonged washing, is no longer soluble in aqueous chlorides, bromides, or iodides of the alkali-metals, but dissolves in hydrochloric and acetic acids, forming solutions which are not affected by boiling. It behaves like the chlorinated compound towards ammonia and caustic potash (F. Rose, *Pogg.* 28, 132; Elsner, *Pogg.* 47, 609). This precipitate was examined also by Mulder (*J. pr. Chem.* 16, 148) and Marchand (*J pr. Chem.* 16, 383).

Orfila (*Toxicologie*, 2, 316), who first recommended albumin as an antidote to corrosive sublimate, regards this precipitate as a compound of calomel with altered albumin, containing 62·22 p. c. of albumin. Bostock found 6 parts of albumin to 1 part of sublimate; Lassaigne, 93·45 p. c. of albumin and 6·55 of sublimate; Elsner, in precipitate *b*, 89·26 p. c. albumin, and 10·74 mercuric oxide. Mulder (*Berzel. Jahresber.* 18, 537) regards the precipitate as a mixture of a compound of albumin with mercuric oxide and hydrochlorate of albumin: after washing, it contains, according to his observations, only 0·4 p. c. of chlorine, in the form of calomel formed by the reduction of the corrosive sublimate (*Pogg.* 44, 444). — The solution formed by treating the washed precipitate with a quantity of saturated solution of chloride of sodium insufficient to dissolve it completely, and filtering (see above), contains the whole of the chlorine as chloride of sodium, and 4·1 parts of chloride of sodium to 1 part of the albuminate precipitate (Voit). Albumin precipitated by fuming hydrochloric acid and redissolved in water, is not precipitated by mercuric chloride from either cold or hot solution (Commaille).

Mercuric chloride in solution, mixed with an equal number of atoms of *chloride of sodium*, precipitates albumin less freely than in the absence of chloride of sodium, and no longer precipitates it at all when 2 atoms of the mercuric chloride are mixed with 3 atoms of the sodium salt (Lassaigne). Albumin containing chloride of sodium has an alkaline reaction after addition of mercuric chloride, which produces no precipitate; on boiling the solution, albumin is thrown down, together with a little mercury (Voit, *Ann. Pharm.* 104, 341).

When a filtered solution of white of egg in its own bulk of water is saturated with neutral salts, mercuric chloride reacts with it as follows:—No precipitate is formed in solutions previously saturated with iodides, bromides, or chlorides of the alkali-metals; solutions saturated with the chlorides of barium, strontium, and calcium, give a turbidity soluble in excess of the albuminous liquid; solutions containing phosphate, sulphate, or nitrate of soda, nitrate of potash, borax, or sulphate of potash, give precipitates, which are for the most part soluble in excess of the albuminous liquid, all soluble in phosphoric acid, ammonia, and potash, and precipitable from these solutions by acetic acid. Solution of albumin saturated with chloride of sodium gives with phosphoric acid a precipitate soluble in excess, and with acetic acid, a precipitate insoluble in excess of the precipitant (Melsens).

Aqueous albumin is not precipitated by *cyanide of mercury* (Bostock).

Albumin produces in solutions of *nitrate of silver* a white precipitate (Bostock) soluble in ammonia (Simon). The precipitate contains 16·15 p. c. of oxide of silver; while moist it turns black in the air, even in the dark. Solutions of nitrate of silver containing a large excess of acid give, on addition of albumin, a precipitate containing 8·9 p. c. of oxide of silver (Mulder).

Terchloride of gold gives with albumin a yellowish, *bichloride of platinum* a yellowish-white precipitate. That produced by the latter in acid solutions of albumin contains, after drying at 100°, 7·97 to 8·77 p. c. of platinum (A. Fuchs, *Ann. Pharm.* 151, 372).

The *platinum-compound* of albumin from fresh eggs contains 9·05 p. c., that from older eggs, 9·33 to 10·15 p. c. of platinum.—When diluted and filtered albumin is precipitated with hydrochloric acid, and the precipitate (that produced at first as well as the second precipitate, which is thrown down by further addition of acid from the solution after standing two hours) is dissolved in water, bichloride of platinum throws down from the solution, compounds containing 10·09 and 10·32 p. c. of platinum. Other platinum-compounds contained 9·30 to 10·32 p. c. (Commaille).

Ferrocyanide of potassium throws down from albumin containing acetic acid, a precipitate free from potash; 1612 parts of albumin require for complete precipitation 211 parts of the ferrocyanide, so that the precipitate is represented by the formula $C^{144}N^{18}H^{112}S^{2}O^{44},H^{2}FeCy^{3}$ (Boedeker, *Ann. Pharm.* 111, 195).

Platinocyanide of potassium produces in dilute solutions of albumin slightly acidified with acetic acid, a pasty precipitate, which soon settles down in white flocks; alkaline solutions are not precipitated (Schwarzenbach). The precipitate is produced only after the conversion of soluble albumin into acid albumin by the acid. When, therefore, acetic acid is added to diluted egg albumin till a precipitate is formed, the acid filtrate gives no precipitate with platinocyanide of potassium, either immediately or on standing; but when a larger quantity of strong acetic acid is added, the platinocyanide immediately throws down a curdy white precipitate, proportionate in quantity to the acid albumin formed.—Albumin acidified with hydrochloric acid gives, on addition of platinocyanide of potassium, a precipitate, which disappears again at first, and likewise dissolves in excess of the precipitant when the solution is alkaline, and in carbonate of soda, and is reprecipitated by acids (Diakanow).

The precipitate is white and curdy; when dried over oil of vitriol, or at 100°, it becomes translucent, like gum tragacanth, and afterwards transparent and glassy. In the dry state it is hard, brittle, and slightly hygroscopic; when heated it evolves an odour of hydrocyanic acid and burnt horn, and leaves 5·56 p. c. of platinum (Schwarzenbach, *Ann. Pharm.* 113, 185; *Chem. Centr.* 1865, 321). The precipitate contains amounts of platinum differing with the time of washing and the kind and quantity of acid present; that precipitated from an acetic solution contained 3·17 p. c., while that thrown down from a solution strongly acidified with hydrochloric acid, contained 1·47 p. c, and with less hydrochloric acid, 6·33 p. c. of platinum. The amount of platinum in a precipitate containing 4·52 p. c. was reduced by prolonged washing to 0·85 p. c. (Diakanow, *Tübing. medic. chem. Untersuch.* 1867, 1, 228). A. Fuchs (*Ann. Pharm.* 151, 372) also found the percentage of platinum to depend upon the time of washing, and to vary according as the platinocyanide or the albumin was in excess at the time of precipitation. Schwarzenbach thinks it probable that the discrepancy between later experiments and his own may be due partly to the use of Quadrat's salt (viii, 48), instead of Gmelin's (*Zeitschr. f. Chem.* [2], vii, 94).

Soluble albumin is coagulated by *alcohol*, both in the dry state and in aqueous solution, and is then, according to Payen & Henry, nearly insoluble in cold, and but slightly soluble in warm ammonia. Lieberkuhn (*Müller's Arch.* 1848, 323) obtained a gelatinous mass by mixing white of egg, diluted with three or four times its bulk of water, with an equal volume of alcohol. But according to J. C Lehmann (*Virchow's Arch.* 36, 116) neutral albumin gives with alcohol a flocculent precipitate, a jelly being obtained only with alkaline or acid solution of albumin, and consisting of sodium albuminate or albumin-acetic acid. See also

Ether free from alcohol gradually converts egg albumin into a white, solid jelly; according to Chevreul, even when the ether has been saturated with water by agitation therewith. The jelly behaves with water like coagulated albumin (Simon). On pouring off the ether and shaking the jelly with water, a liquid is obtained, which is precipitated by alcohol, and therefore still contains albumin (Fauré, *J. Pharm.* 21, 467).

Dilute solution of white of egg is rendered turbid by the addition of 1 p. c. of *carbolic acid*, and afterwards coagulates. The coagulum does not putrefy in the air. A portion of the albumin remains in solution.— *Cresylic alcohol* acts in a similar manner, but more slowly. (*Oesterr. Vereinzeitschr.* 1868, 477).

Oil of turpentine, even when free from acid, causes the white of ducks' eggs to coagulate (Chevreul). A solution of one drop of the white of hen's egg in 8 ounces of water, when mixed with two or three drops of oil of turpentine, becomes opalescent, and deposits coagulated albumin. A similar effect is produced by *petroleum* and other *volatile oils*, and even by distilled waters containing volatile oils (Lienan, *Polyt. Notizbl.* 19, 231). Water which has been shaken with *camphor* coagulates albumin (Lightfoot, *Polyt. Notizbl.* 19, 112). See also Monoyer (*Par. Soc. Bull* [2], 5, 444).

When an aqueous solution of albumin, slightly acidified with mineral acids and thereby rendered clear, is mixed with *dextrin*, whether formed by the action of diastase or of acids, there is produced a flocculent precipitate, which is insoluble in excess of dextrin and in acids. When proper proportions of the two substances are employed, the filtrate is not precipitable either by albumin or by dextrin. — The amount of precipitate is larger when as much as 6 parts of dextrin is employed to 1 part of albumin than with a smaller proportion. The precipitates dried at 115° contain 13·3 to 14·2 p. c. of nitrogen, and appear, therefore, not to consist of pure albumin. — Acidified albumin is precipitated by *gum arabic*, an excess of which redissolves the precipitate, forming a solution which coagulates when heated even in presence of any quantity of organic acid (Günsberg, *Wien. Acad. Ber.* 45, 643; 49, 409; *Chem. Centr.* 1863, 460; 1865, 72; *Kopp's Jahresber.* 1863, 571; 1864, 621).

When aqueous albumin is mixed with *tannic acid* a yellow pitchy precipitate is obtained (Provost). On adding a little tannic acid to a large quantity of albumin, a clear liquid is obtained, which is coloured blue by ferric salts (Quevenne, *J. Pharm.* 22, 452). The precipitate has a varying composition (Mulder).

Albumin is not coagulated by *rennet* at ordinary temperatures.

Albuminic Acid.

LIEBERKÜHN. *Pogg.* 86, 117, and 298; *J. pr. Chem.* 57, 352; *Kopp's Jahresber.* 1851, 692.

Moderately strong aqueous alkalis produce with all albuminous substances, bodies called *albuminates*, or salts of *albuminic acid*, which exhibit reactions in common, and agree in composition and chemical properties with the casein of milk, but differ in their action on polarised light according to their origin.

According to Kühne, albuminates occur in animal fluids, especially in the serum of blood and in serous liquids. When blood-serum diluted with ten times its volume of water is freed from paraglobin by precipitation with carbonic acid, a trace of acetic acid added to the liquid decomposes albuminate of soda, and throws down albuminic acid as a white pulverulent body, which is insoluble in oxygenated water, and very slowly soluble in neutral salts of the alkalis, but dissolves easily in dilute acids and alkalis (Kühne). J. C. Lehmann (*Virchow's Arch.* 36, 125) doubts the occurrence of albuminate of soda in the blood; Brücke found the precipitate produced by Kühne's method to be easily and completely soluble in chloride of sodium, forming a solution which coagulated like albumin when heated. See also *Serum albumin*, p. 275.

When egg albumin diluted with three or four volumes of water, and made slightly alkaline with caustic soda, is mixed with an equal volume of alcohol, a gelatinous mass of albuminate of soda is obtained, which in other respects behaves like albuminate of soda prepared without alcohol, but melts when warmed, and solidifies again as it cools. 1 c.c. of a neutral solution of albumin mixed with one drop of 2 p. c. soda-ley and alcohol forms this jelly, which is not produced with a larger quantity of alkali (J. C. Lehmann, *Virchow's Arch.* 36, 115).

Free *albuminic acid* precipitated from albuminate of potash by acetic acid, and by phosphoric or other mineral acids, resembles coagulated albumin (Lieberkühn).

Albuminic acid dried at 130°.			Lieberkühn.	
			a.	*b.*
72 C	432	53·59	53·51	53·15
9 N	126	15·65	15·61	15·88
56 H	56	6·95	7·03	7·13
S	16	1·98	1·83	
22 O	176	21·83	22 02	
$C^{72}N^{9}H^{56}SO^{22}$	806	100·00	100·00	

a was precipitated by acetic, *b* by phosphoric acid. Free from phosphorus and ash. — To this place belongs a product obtained by Fleitmann, described under egg albumin (p. 295).

When egg albumin, mixed with $\frac{1}{10}$th of hydrate of soda or potash is submitted to dialysis, *albuminic acid soluble in water* is obtained, the alkali alone passing through the dialyser. This albuminic acid precipitates Graham's colloidal silicic acid; it throws down from solutions of emulsin a white pulverulent precipitate soluble in acetic acid (Graham, *Ann. Pharm.* 121, 61; *Kopp's Jahresber.* 1861, 80) Soluble albuminic acid is not obtained by precipitating albuminate of potash with basic acetate of lead and decomposing the precipitate with carbonic acid (Lieberkühn).

Albuminate of Potash. — Albumin, when triturated with strong potash-solution, is converted, after some time, into a jelly, which becomes transparent and brittle in the air (Thomson).

Preparation. White of hens' eggs is cut up with scissors and shaken vigorously with air, whereupon the membranes rise to the surface with the froth. It is then diluted with water and filtered, and the filtrate is evaporated to the original volume, and mixed with strong potash-solution, which converts it into a translucent, yellowish, very elastic mass. This is cut into pieces of the size of beans, and washed with water so long as the liquid acquires an alkaline reaction. The swollen residue forms a turbid liquid on boiling with water or alcohol, and dissolves completely, provided access of air [carbonic acid (Brücke)] has been prevented as far as possible during washing (Lieberkühn). When the washing is continued till the transparent pieces begin to appear milky at the edges, they are still soluble in boiling water, but after very prolonged washing the pieces become opaque, and are then insoluble in boiling water (Kühne, *Physiol. Chemie*, 175). This effect is due to carbonic acid in the water; in water free from carbonic acid the pieces melt from without inwards and dissolve (Brücke).

When a solution of albumin gelatinised by potash is treated several times with water, and afterwards boiled with alcohol, a solution is obtained, from which ether throws down a precipitate of albuminate of potash soluble in boiling water and alcohol; when dried, the precipitate becomes insoluble in both liquids, and is converted into an amber-yellow mass, difficult to powder. This mass, after washing with water, which still takes up potash, has the following composition (Lieberkühn).

	Dried at 130°.		Lieberkühn.
72 C	432	50·63	50·21
9 N	126	14·79	
56 H	56	6·56	6·65
22 O	176	20·63	
S	16	1·87	
KO	47·1	5·52	5·44
$C^{72}N^9H^{56}SO^{22},KO$	853·1	100·00	

1 part of soda combines with 4 parts of albumin to form albuminate of soda (v. Wittich).

Aqueous albuminate of potash does not coagulate at 140° (Hoppe-Seyler). — Solutions of alkaline albuminates, when carefully neutralised by *acids*, deposit the albuminic acid, which dissolves in excess of acids (Lieberkühn).

When solid albuminate of potash, cut in pieces, is immersed in so much aqueous *acid phosphate of lime*, or *phosphoric*, *boracic*, *hydrochloric*, or *acetic acid*, that the liquid still retains an acid reaction, the albuminate turns milk-white, begins to shrink, and solidifies to an elastic mass. The substance thus formed is Brücke's *Pseudofibrin;* it swells up to a glassy jelly, without dissolving, in water containing $\frac{1}{10}$th p. c. of phosphoric, acetic, or hydrochloric acid; dissolves easily in potash-solution; and swells up, becomes opaque, and dissolves in ammonia, from which it is precipitated by neutralisation (Brücke, *Virch. Arch.* 12, 193. — *Wien. Acad. Ber.* 2 Abth. 55, 881; *Chem. Centr.* 1867, 1005).

Carbonic acid also precipitates all alkaline albuminates (v. Wittich; J. C. Lehmann). It does not precipitate the natural albuminates (Kühne, p. 274). *Boracic acid* precipitates aqueous albuminate of potash completely (Brücke). *Nitric acid* throws down a precipitate which dissolves in the slightest excess of the acid, re-appears on adding more acid, dissolves on boiling, and is deposited in the form of a jelly as the solution cools. When *acetic acid* is added to a neutral solution of albuminate of potash till the precipitate formed at first just disappears, the solution coagulates on boiling, or on addition of alcohol. On evaporating a solution containing excess of acetic, *lactic*, or *phosphoric acid*, there remains a residue, a solution of which in boiling water forms pellicles when evaporated, is precipitated by acetic acid (the precipitate dissolving in excess) and does not coagulate when heated, behaving, therefore, like casein (Lieberkühn).

When the alkaline solution of albumin has been boiled, the precipitate produced in it by acetic acid is no longer soluble in excess of the acid. Sal-ammoniac precipitates the alkaline solution on boiling, and likewise precipitates a previously boiled solution in the cold (Gorup-Besanez, *Ann. Pharm.* 125, 122). An aqueous solution of albuminate of potash, to which a large quantity of chloride of sodium has been added, is precipitated on warming (Lieberkuhn, *Virchow's Arch.* 5, 162).

The albuminic acid thrown down from alkaline solutions by acids dissolves easily in dilute acids and alkalis, and in aqueous solutions of neutral salts of the alkalis containing as much as 10 per cent. of the salts, provided it has not remained long under water or been boiled with water. The saline solutions are syrupy, and are precipitated by addition of water or acids, and by a boiling heat. Albuminic acid which has been boiled with water is insoluble in saline solutions and dilute acids; after being precipitated from alkaline solutions by acids, and left for some time under water, it dissolves with difficulty, and only when heated, in hydrochloric acid of 0·1 per cent. Albuminic acid is converted into syntonin in all acid solutions, so that the precipitate thrown down from these solutions on neutralisation is insoluble in neutral salts, and soluble only in caustic alkalis and their carbonates (Kühne, *Physiol. Chemie,* 176). Brücke (*Wien. Acad. Ber.* 2, Abth. 55, 881; *Chem. Centr.* 1867, 1003), found the precipitate produced in alkaline solutions of albumin on neutralisation to be insoluble in saline solutions, and more easily soluble in acids in proportion as the liquid was more free from salts.

When a solution of coagulated albumin in the smallest possible quantity of potash-solution, to which acetic acid is added till the precipitate disappears, is submitted to dialysis till it is no longer acid, there is left a slightly opalescent liquid which coagulates when heated and is precipitated by mineral acids, small quantities of alkalis, and neutral salts, and hence contains the albumin (albuminic acid) in a form analogous to that of Graham's soluble silicic acid (Schützenberger, *Par. Soc. Bull.* 1, 285; 5, 163). See also Hoppe-Seyler (*Anal. Zeitschr.* 3, 427).

The presence of *alkaline phosphates* in solutions of albuminate of potash prevents, to a certain extent, the precipitation by acids, including carbonic (Kühne; J. C. Lehmann) and boracic acids (Brucke), so that solutions are obtained which redden litmus, and, after addition of more acid, throw down a precipitate soluble in excess of the acid. When albuminate of potash is mixed with phosphate of soda or potash and then with dilute acids (acetic, lactic, phosphoric, hydrochloric, or nitric), drop by drop, till the solution exhibits an acid reaction and begins to appear opalescent, the addition of ferrocyanide of potassium produces no precipitate. The solution rendered opalescent by a rather larger quantity of acid, does not undergo alteration at ordinary temperatures; it becomes turbid on heating, but still contains albumin in solution at 100°. When, on the contrary, a solution of albuminate of potash containing alkaline phosphate is mixed with sufficient acid to redissolve the precipitate first produced, a solution is formed from which ferrocyanide of potassium throws down an abundant precipitate. Further, when dilute acids are added to albuminate of potash till insoluble albumin begins to be thrown down, the addition of phosphate of soda produces an acid solution which is not precipitated by ferrocyanide of potassium (Rollet, *Wien. Acad. Ber.* 39, 547; *Chem. Centr.* 1860, 433).

Albuminate of soda is not coagulated by rennet (Lieberkühn).

Albuminate of Baryta.—Precipitated by chloride of barium from alcoholic (not from aqueous) albuminate of potash, as a mass resembling coagulated albumin. Free from hydrochloric acid (Lieberkühn).

	Dried at 130°.		Lieberkühn.
144 C	864	50·90	50·59
113 H	113	6·66	6·83
18 N	252	14·84	
45 O	360	21·21	
2 S	32	1·88	
BaO	76·5	4·51	4·44
$2(C^{72}H^{56}N^{9}O^{22}S).BaOHO$	1697·5	100·00	

Aqueous albuminate of potash coagulates when boiled with *chloride of calcium* (Lieberkühn).

Albuminate of Zinc.—Precipitated by sulphate of zinc from aqueous albuminate of potash. Yellow, friable precipitate, insoluble in alcohol (Lieberkühn).

			Lieberkühn.
72 C	432	51·02	50·37
56 H	56	6·61	6·62
9 N	126	14 90	
22 O	176	20 79	
S	16	1·89	
ZnO	40 5	4·79	4·66
$C^{72}H^{56}N^{9}O^{22}S,ZnO$	846 5	100·00	

Basic acetate of lead and *nitrate of lead* throw down from albuminate of potash, white precipitates insoluble in water. When decomposed with carbonic acid, they yield no soluble albumin (Lieberkühn).

Albuminate of Copper.—Sulphate of copper throws down from albuminate of potash a precipitate which is insoluble in water and alcohol, and dries up to a green brittle mass. It is decolorised by warm acids, without dissolving (Lieberkühn).

	Dried at 130°.		Lieberkühn.
72 C	432	51·07	50·86
56 H	56	6·62	6·83
9 N	126	14·92	
22 O	176	20·81	
S	16	1·89	
CuO	39·7	4·69	4·61
$C^{72}H^{56}N^{9}O^{22}S,CuO$	845·7	100·00	

Albuminate of Silver.—Nitrate of silver throws down from albuminate of potash, white flocks which dissolve in nitric acid and blacken on exposure to light (Lieberkühn).

	Dried at 130°.		Lieberkühn.
144 C	864	49·73	49·61
113 H	113	6·51	6·66
18 N	252	14·53	
45 O	360	20·72	
2 S	32	1·84	
AgO	116	6·67	6·55
$2(C^{72}H^{56}N^{9}O^{22}S),AgO,HO$	1737	100·00	

A. Fuchs (*Ann. Pharm.* 151, 372) found 3·29 per cent. of silver in the salt dried at 100°.

Casein.

SCHEELE. *Opusc.* 2, 101. — FOURCROY & VAUQUELIN. *N. Gehl.* 2, 638. — BERZELIUS. *Schw.* 11, 277; *Lehrb.* 3, Aufl. 9, 676. — SCHÜBLER. *Schw.* 19, 458. — BRACONNOT. *Ann. Chim. Phys.* 35, 159; 43, 337.
MULDER. *J. pr. Chem.* 17, 333; 20, 340. — *Berzel. Jahresber.* 26, 910.
SCHERER. *Ann. Pharm.* 40, 1.
DUMAS & CAHOURS. *N. Ann. Chim. Phys.* 6, 411.
ROCHLEDER. *Ann. Pharm.* 45, 251.
SCHLOSSBERGER. *Ann. Pharm.* 58, 92; *Berzel. Jahresber.* 27, 636.
BOPP. *Ann. Pharm.* 69, 16; *Pharm. Centr.* 1849, 241; *Jahresber.* 1849, 491.
LIEBERKÜHN. *Pogg.* 86, 117 and 298; *Jahresber.* 1852, 692.
F. HOPPE-SEYLER. *Virchow's Arch.* 17, 417; *Chem. Centr.* 1860, 49 and 65; *Jahresber.* 1859, 627. — *Krit. Zeitschr.* 1864, 737; *Anal. Zeitschr.* 3, 424; *Jahresber.* 1864, 614.
MILLON & COMMAILLE. *Compt. rend.* 59, 301; *N. J. Pharm.* 46, 273; *Chem. Centr.* 1865, 428; *Jahresber.* 1864, 622. — *Compt. rend.* 60, 118 and 859; 61, 221; *J. Pharm. Chim.* [4] 1, 204; 2, 144 and 278; *Jahresber.* 1865, 643. — COMMAILLE. *Réceuil des mémoires de méd. militaire* [3] 17, 145 and 249; *Chem. Centr.* 1867, 588.

Casein is the name given to the proteide which occurs in the milk of mammals, in especial abundance in that of carnivorous animals, and, as a rule, predominates over the other proteides. According to Fr. Simon (*Die Frauenmilch*, Berlin, 1838; *Berzel. Jahresber.* 1839, 714) the casein of human milk is different from that of cow's milk.

This proteide is regarded either as a peculiar substance, or as identical with serum-albuminate of potash.

The latter view is supported by the fact that all the albuminous reactions of milk are exhibited by artificial solutions of albuminates of the alkalis; also by the occurrence (disputed, however, by Brücke, Eichwald, and others) of small quantities of alkaline albuminates, not only in milk, but in all albuminous animal fluids. The reactions described as peculiar to casein are comprehensible when it is remembered, on the one hand, that milk contains, besides albuminate of potash, phosphate of potash, and a number of substances capable of yielding free acids by fermentation; and, on the other hand, that the behaviour of alkaline albuminates is essentially modified by the presence of alkaline phosphates (Kühne, *Physiol. Chemie*, 565). Hoppe-Seyler (*Handbuch.* 188) considers the identity of the two bodies to be disproved by their action on polarized light. Strong potash-solution increases the rotatory power of serum albumin to 86°, and that of casein to 91°. Moreover, casein dissolved in potash-solution, and precipitated therefrom by acetic acid, cannot be distinguished from natural casein, although the smell of hydrosulphuric acid evolved in the process shows that the two differ. Although both these grounds appear to me to be inconclusive, the separate treatment of the two substances seems to be expedient in this work (Kr.).

Milk contains, especially at the commencement of lactation, a second proteide, which is generally described as albumin (p. 274). The separation of this milk-albumin from casein is specially provided for in the first two only of the following methods of preparation.

Preparation. 1. Milk is saturated with crystallised sulphate of magnesia; the thick white mass of precipitated casein is collected, washed with saturated solution of sulphate of magnesia, and dissolved in a volume of water equal to the milk employed; the fat is separated by filtration; and the colourless filtrate is evaporated at 40°, whereupon casein containing sulphate of magnesia separates in lumps (Denis).— 2. New milk is diluted to 20 times its bulk with water, and weak acetic acid is dropped into it, with constant stirring, till a flocculent precipitate begins to form. Carbonic acid is then passed through it for a quarter or half an hour, after which it is left to itself for a few hours or a day. The casein, mixed with butter, then goes down as a fibrous flocculent precipitate, which is separated by filtration, washed, and freed from butter by means of alcohol and ether (Hoppe-Seyler, *Handbuch.* 357).

3. Diluted milk is mixed with hydrochloric acid till a copious coagulum and a clear yellowish liquid are produced. The precipitate is washed with water containing 2 or 3 per cent. of hydrochloric acid, and then with pure water, till it becomes gelatinous, and is afterwards diffused through water at 40°. From the solution thus formed. alkaline carbonates throw down casein which is easily washed (Bopp).

4. Milk is warmed with dilute sulphuric acid; the coherent curdy mass which is precipitated is kneaded under water repeatedly, and treated with a slight excess of a strong aqueous solution of carbonate of soda; and the turbid liquid thereby formed is allowed to stand in shallow vessels, till the butter separates in the form of a floating layer. After removing this last, the solution is precipitated with dilute sulphuric acid; the precipitate is purified by kneading it under water; and this process of dissolving and precipitating is repeated three times. The casein thus obtained still contains sulphuric acid (and hence is partially soluble, especially in warm water, forming a solution, which yields it in pellicles on evaporation, and in flocks when neutralised with carbonate of soda), from which it is freed by boiling it 15 or 20 times, with 60 to 70 parts of water. Lastly, it is boiled with alcohol and ether, to free it from substances soluble in those liquids (Rochleder).

5. Milk is coagulated at the boiling-heat by means of acetic acid, and the casein thrown down is washed with hot water, alcohol, and ether. Or the casein is dissolved in moderately dilute solution of carbonate of soda; the solution is left at rest till the butter separates, then precipitated with acetic acid; and the precipitated casein is purified as above (Rüling). Similar processes were adopted by Mulder and by Dumas & Cahours.

6. Milk is mixed with a saturated solution of chloride of sodium; the coagulum of casein thereby thrown down is washed with alcohol and ether, and dissolved in weak ammonia; the solution is precipitated with acetic acid, and the precipitate is washed with cold water, alcohol, and ether (A. Völckel, *J. pr. Chem.* 71, 118).

According to Mulder (*Berzel. Jahresber.* 26, 910) casein may be separated into two distinct substances, one of which is precipitated from the solution of hydrochlorate of casein by carbonate of ammonia, whilst the other is thrown down from the filtrate only on addition of hydrochloric acid. Further, the former is thrown down from buttermilk by hydrochloric acid, the latter only on boiling the filtrate. Schlossberger (*Ann. Pharm.* 58, 92) confirms Mulder's statement, and believes that only the casein precipitated by carbonate of ammonia contains sulphur, not that which is thrown down from the filtrate by hydrochloric acid. Bopp (*Ann. Pharm.* 69, 16), however, found sulphur both in the casein free from chlorine thrown down by carbonate of ammonia, and in that containing chlorine precipitated by hydrochloric acid; in neither case is the sulphur recognisable on heating with potash and oxide of lead. When soluble hydrochlorate of casein is precipitated by carbonate of ammonia and filtered, the filtrate is still precipitable by hydrochloric acid, either because it contains casein-ammonia, owing to too much, or hydrochlorate of casein, owing to too little carbonate of ammonia having been added (Bopp).

Millon and Commaille distinguish a casein suspended in milk, and another dissolved in it, the former being said to contain 14·87, the latter 17·18 p. c. of nitrogen. On diluting new milk with water, and filtering, the suspended casein is said to remain on the filter with the cream. The amount of soluble casein decreases rapidly on standing, so that milk diluted with water and allowed to become sour contains no casein, but only albumin in solution. Millon & Commaille afterwards (*J. Pharm. Chim.* [4], 2, 144) gave for soluble casein the formula, $C^{108}N^{14}H^{97}O^{29}$ + 5 aq., the insoluble being stated to contain 2 atoms of water less. Casein dried over oil of vitriol loses 2·21 p. c. (= 3 atoms) of water at 115°, and 3·71 p. c. (= 5 atoms) at 150°. All these statements, as well as the formula (calc. 55·24 p. c. C., 16·71 N., 8·27 H., 19·78 O.), which takes no account of the sulphur, appear to contain but little that is true (Kr.).

Properties. Amorphous, yellowish, hygroscopic mass, without taste or smell. — According to Rochleder, it reddens litmus, without giving up acid to water.

Rotates a ray of polarised light to the left; $[\alpha]j$ for casein dissolved in aqueous sulphate of magnesia, is equal to − 80°; in very weak hydrochloric acid, − 87°; in slightly alkaline solution, − 76°; in strongly alkaline solution, − 91° (Hoppe-Seyler, *Handbuch der physiol. Anal.* 1865, 191).

	Mulder.		Scherer.				
	1.	2.	3.	4.	5.	6.	7.
Dried at	130°.	130°.	100°.	100°.	100°.	100°.	100°.
C	54·21	54·68	55·57	54·13	54·00	53·89	53·79
H.	7·15	7·31	7·63	7·15	7·35	7·35	6·93
N	5·80	14·00	15·87	15·63	15·72	15·40	15·67
Ash deducted	3·83	00		10	2·00	1·50	2·00

	Rochleder.		Dumas & Cahours.				
	8.	9.	10.	11.	12.	13.	14.
			Cow.	*Goat.*	*Ass.*	*Sheep.*	*Woman.*
Dried at	145°.	100°.	140°.	140°.	140°.	140°.	140°.
C	53·43	52·63	53 50	53·60	53·66	53·52	53·47
H	7·11		7·05	7·11	7·14	7·07	7·13
N			15·77	15·78	16·00	15·80	15·83
Ash deducted	0·30		1·00	5·46	0·96	1·20	4·86

	Rüling.		Völckel.
	15.	16.	17.
	140°.	140°.	140°.
C	53·35	53·71	53·43
H	7·11	7·09	7·12
N			15·36
Ash deducted	1·40		0·32

Remarks on the analyses.—1. Mulder's casein (1) was precipitated by acetic acid; 2 by heat from buttermilk. The sulphur determinations—0·36 and 0·10 p. c. respectively—were made by dissolving the casein in nitric acid, and precipitating with baryta, and are therefore erroneous; so are probably also the phosphoric acid determinations, according to which (1) contained 3·50, while (2) contained 1·35 p. c. of phosphoric acid. The casein of butter-milk is, according to Mulder, altered casein. 3—7 Scherer analysed (3) the pellicle of casein formed on evaporating milk; (4) casein precipitated by alcohol; (5) the coagulum produced on heating sour uncurdled milk; (6) casein precipitated by acetic acid, and purified by dissolving it in carbonate of soda and reprecipitating with acetic acid, (7) that portion of the casein of milk which remains in solution when milk turns sour, and coagulates on boiling. In all cases the casein was purified by exhaustion with boiling alcohol and ether.—8 and 9. Rochleder's analysis (8) gives the mean percentages of carbon and hydrogen contained in casein precipitated from sulphuric solution by sulphuric acid, by acetic acid; and by carbonate of soda; (9) is the same, but dried at 100° for three days.

10—14 Dumas & Cahours precipitated their casein at the boiling-heat by acetic acid, excepting that from human milk, which was precipitated by alcohol.—15 and 16. Rüling's casein. (15) was obtained from new milk, (16) from new cheese. Völckel's casein contained also 0·74 p. c. of phosphorus.

The proportion of sulphur in casein was found to be 0·85 to 1·017 p. c. (Rüling, *Ann. Pharm.* 58, 319), 0·843 p. c. (Verdeil, *Ann. Pharm.* 58, 319), 0·933 p. c. (Walther, *Ann. Pharm.* 58, 315), 1·11 p. c. (Völckel), and, lastly, 0·9 to 1·1 p. c. (Schwarzenbach, *Ann. Pharm.* 133, 191). Hence, as Schwarzenbach points out, casein contains half as much sulphur as egg albumin.

From the experiments of Lubavin (*Med.-chem. Unters.* 1871, 463), it appears that casein, like vitellin or hæmoglobin, is a compound of an albuminous or proteid compound with a non-albuminous body. When digested with artificial gastric juice, it yields a body containing phosphorus, whereas albuminate can be prepared from white of egg, which contains no phosphorus: hence casein is not identical with albuminate prepared from the other albuminous bodies. (See p. 303—306.)

Decompositions. 1. Curd thrown down by rennet and dried yields by *dry distillation* the same products as gelatin, leaving charcoal containing phosphates (Schübler; Berzelius).—2. *Ozonised air* passed into solution of casein produces neither precipitate nor coloration, but when the current is continued for some time, the solution becomes coagulable by boiling or by nitric acid. Afterwards the albuminous substance thus coagulable is also destroyed, and there then remain the same products as are formed in the case of albumin (Gorup-Besanez, *Ann. Pharm.* 110, 100).—3. Casein subjected to prolonged boiling with water, with access of air, or heated to 108° with water, yields the same products as syntonin similarly treated, namely parapeptone, peptone, and small quantities of lactic acid and creatinine (Meissner, *Zeitschr. für. ration. Medic.* [3] 10, 18). When casein is heated to 135° with water in a sealed tube for 5 hours, it is converted into a yellow mass, above which is a yellow acid liquid. The latter gives with Millon's mercury-solution the reaction of proteides, and does not contain any peptones (W. Schmidt, *Anal. Zeitschr.* 8, 131).

4. Casein heated with *binoxide of manganese* and *dilute sulphuric acid*

is dissolved to a frothing liquid, and evolves volatile products consisting of acetic, propionic, and butyric aldehydes, oil of bitter almonds, and several volatile acids, viz., formic, acetic, propionic, butyric, valerianic, caproic, and benzoic acids, but no hydrocyanic acid. — A mixture of *bichromate of potash* and *sulphuric acid* forms large quantities of hydrocyanic acid, no aldehyde, a trace of bitter almond oil, propionic aldehyde, valeronitrile, a heavy neutral oil having an odour of cinnamon, and the same volatile acids as are obtained with binoxide of manganese and sulphuric acid, with the exception of caproic acid, the presence of which is doubtful (Guckelberger, *Ann. Pharm.* 64, 39). Chromic acid throws down from solutions of casein a dark-yellow coagulum, which behaves towards acids and alkalis in the same way as the precipitate similarly obtained from solutions of albumin (Hühnefeld, *J. pr. Chem.* 9, 30). — Milk diluted with water and acidified decolorises *permanganate of potash*, owing to the casein and albumin contained in it (Monier, *Compt. rend.* 46, 236, and 425).

5. When *chlorine* is passed through aqueous casein-ammonia, white flocks of protein-chlorous acid are precipitated; the acid filtrate contains a little humin and salts (Mulder). — 6. *Nitric acid* dissolves cheese with yellow colour, forming Mulder's xanthoproteic acid. — 7. Curds precipitated by rennet dissolve in hot *oil of vitriol* with dark-red colour, forming a solution which gives with water at first a white, but after some weeks a dirty-brown precipitate (Schübler). Casein forms with oil of vitriol a transparent jelly, from which water throws down casein-sulphuric acid (Mulder). Moderately dilute sulphuric acid decomposes casein in the same way as hydrochloric acid (Bopp). The products of decomposition include aspartic acid (Kreussler, *J. pr. Chem.* 107, 240).

8. Casein dissolves in 4 to 5 parts of strong hydrochloric acid with fine violet colour, gradually turning brown on exposure to air. When the solution is boiled for 6 or 8 hours and evaporated, there remains a dark viscid syrup, which contains, of crystallisable substances, leucine, tyrosine, and leucimide; the non-crystallisable portion tastes sweet, does not undergo fermentation with yeast, evolves hydrosulphuric acid when boiled with potash and afterwards acidified with acetic acid, and forms a violet solution with potash and sulphate of copper (Bopp). Schübler had previously noticed that curds thrown down by rennet dissolved with blue colour in hydrochloric acid.

9. When casein precipitated by acetic acid is dissolved in *potash-ley*, the alkaline solution does not blacken acetate of lead, or evolve hydrosulphuric acid when mixed with acids, but both these effects are produced after the alkaline solution has been boiled (Liebig, *Ann. Pharm.* 57, 131). Scheele noticed the evolution of hydro-sulphuric acid produced by acids in solutions of casein in potash-ley. — By digesting the alkaline solution with hydrate of bismuth for 6 or 8 hours, at a temperature near the boiling-heat, sulphur amounting to 0·07 per cent. of the casein is obtained in the form of sulphide (Fleitmann, *Ann. Pharm.* 66, 380). The precipitate thrown down (with evolution of hydrosulphuric acid) by acetic acid from a solution of casein in weak potash-ley (Mulder's protein) contains at 140°, after deducting 1·43 p. c. of ash, 53·46 p. c. C., 15·94 N., and 7·10 H. (Dumas & Cahours, *N. Ann. Chim. Phys.* 6, 420).

On heating a solution of casein in weak potash-ley till the precipitate produced by acetic acid in a hot test-portion of the liquid melts to a resinous mass and dissolves in alcohol, and then precipitating the hot solution with acetic acid, there is thrown down a white or yellow viscid body, which is nearly free from sulphur, and afterwards hardens to a yellowish-brown mass in the air. This body dissolves in water and is precipitated from the solution by acids; it forms with boiling alcohol a turbid liquid, from which it is deposited again on cooling. Boiling baryta-water dissolves it, forming a crystalline and an amorphous compound, from solutions of which acids throw down a curdy precipitate (Laskowski, *Ann. Pharm.* 58, 160).

When casein is melted with its own weight of hydrate of potash, according to xiii, 359, till not only ammonia but also hydrogen is evolved, the following products are formed: tyrosine, leucine, and, as decomposition-product of the latter, valerianic acid (or by prolonged fusion, butyric acid); also oxalic acid and a volatile substance which smells like fæces and reduces oxide of silver, but no formic acid (Liebig, *Ann. Pharm.* 57, 127; Bopp *Ann. Pharm.* 69, 20). Leucine is formed very early, tyrosine only later (Bopp).

10. When casein covered with water is exposed to the air for several months in summer, *putrefaction* takes place, and the following volatile bodies are formed: carbonic acid, hydrosulphuric acid, ammonia, butyric acid, valerianic acid, and an oily body easily alterable by air or by acids; leucine is also formed as a non-volatile product. A portion of the casein dissolves under the influence of the ammonia produced (Iljenko, *Ann. Pharm.* 63, 264; *Kopp's Jahresber.* 1847 and 1848, 839). Similar observations were made by Bopp. See Albumin. Braconnot (*Ann Chim. Phys.* 35, 159), and Proust (*Ann. Chim. Phys.* 10, 29) previously investigated the products formed by the putrefaction of cheese (not pure casein). See *Leucine* xi, 425. — Even in the ripening of cheese, the casein becomes altered, with formation of ammonia and leucine, but it is not converted into fat as stated by Blondeau. See Blondeau (*Compt. rend.* 25, 360; further *Ann. Chim. Phys.* (4, 1, 208); Brassier (*Ann. Chim. Phys.* (4) 5, 270; *Chem. Centr.* 1865, 888). In a strongly smelling Limburg cheese, Iljenko and Laskowski (*Ann. Pharm.* 55, 78) found volatile fatty acids and unaltered casein. — On addition of carbonate of ammonia or of chalk, the putrefaction of casein proceeds in the same way as that of fibrin (Brendecke).

When milk is milked into glass vessels which are immediately closed air-tight, it deposits, after some time only, a coagulum which afterwards re-dissolves, so that the then nearly colourless liquid contains only butter and a little coagulated casein undissolved. The acid filtrate obtained after two years' standing does not behave like a solution of casein when evaporated; it is precipitated on heating by sal-ammoniac, chloride of sodium, chloride of potassium, sulphate of soda, sulphate of potash, and saltpetre; the precipitates formed by the same salts at low temperatures are soluble in water and not afterwards coagulable by heat (Sullivan, *Phil. Mag.* [4] 18, 203; *J. pr. Chem.* 79, 140).

11. On adding to milk, at 30° to 38°, $\frac{1}{500}$th to $\frac{1}{400}$th of *rennet* (that is, the mucous membrane of the stomach of a sheep or calf freed from liquid, dried, and again softened in water), it deposits the casein, after

the lapse of a few hours, in the form of a coherent tremulous jelly (ordinary cheese), which, after pressing, is white and elastic, and readily cakes together (Schübler). In this process there remains in solution a body precipitable by acetic acid at 75° to 100°, which Schübler distinguished from casein as *Zieger*. Gmelin, Bergsma, Berzelius, and Fr. Simon agree in regarding *Zieger* as casein, which is retained in solution, according to Bergsma, by free acid, or, according to Simon, by alkali. — The casein of Denis is not coagulated by rennet, except after addition of whey.

According to Simon, rennet acts by first forming lactic acid, which then decomposes the casein-alkali of the milk: hence the formation of curds and the acidification of the liquid take place simultaneously at 37° to 43° (Simon). According to Selmi (*N. J. Pharm.* 9, 265; *Berzel. Jahresber.* 27, 635), however, solutions of oxalate and acetate of casein are likewise coagulated by rennet; whilst milk having an alkaline reaction, or mixed with alkali, yields alkaline curds and alkaline whey, when heated to 50° or 56° with rennet. Heintz (*Zoochemie*, 687) found both these statements to be correct, the difference in the results of experiment being due to differences in temperature. Milk is rendered acid by rennet at about 40°, but at 54° to 62° it may be coagulated without being rendered acid. According to Kühne (*Physiol. Chemie*, 567), a partial separation only of the casein took place in these experiments, such as is produced by the smallest quantity of acid at these high temperatures, the liquid again acquiring an alkaline reaction. See also Klunk (*Dissert. über die Coagulation der Milch durch Labflussigkeit*, Giessen, 1863; *Jahresber.* 1863, 648).

The coagulation of milk takes place the more rapidly the longer the rennet has been in contact with air and water; the mucous membrane when perfectly fresh is almost without action. — Curds coagulated by rennet are insoluble in alkaline carbonates, or dissolve only after prolonged boiling, owing to the presence of phosphates of lime and magnesia. When treated with sulphuric acid, they deposit the earthy phosphates (Liebig, *Handwörterbuch*, 3, 229).

Combinations. Casein is insoluble in *water*. The soluble casein of the older chemists is mostly casein-alkali. One part of Rochleder's casein remained in solution in 422 parts of cold water, when the solution was prepared by boiling.

With Acids. — Solutions of casein in alkalis are precipitated by acids, with the exception of carbonic acid (Rochleder), and phosphoric acid (Braconnot). In the absence of alkaline phosphates, they are precipitated by neutralisation with acids; in presence of phosphates an excess of acid is necessary.

All precipitates thrown down by acids from alkaline solutions of casein (including those produced by hydriodic, perchloric, sulphocyanic, and acetic acids), are compounds of casein with the acids; they are all decomposed by water, the acetic acid compound most easily. On dissolving the compound of casein with an acid in aqueous alkali and adding another acid in excess, the casein goes down with the latter, or with both acids together. Thus, when sulphate, phosphate, oxalate, or arseniate of casein is dissolved in alkali, and nitric acid is added to the solution, nitrate of casein is precipitated; and conversely, sulphate of casein is thrown down by sulphuric acid from an alkaline solution of the nitrate (Millon & Commaille, *J. Pharm.* [4], 1, 24).

These compounds have the following formulæ, in which casein, $C^{108}N^{14}H^{97}O^{29}$ (according to Millon & Commaille), is represented by the symbol Cas (Millon & Commaille, *J. Pharm. Chim.* [4] 1, 204):—

Phosphate of Casein. Cas, PO^5 + 4aq. Gives off the water at 130°.—When digested with moderately dilute sulphuric acid, it is converted into sulphate.

Sulphate of Casein. Cas, SO^3 + 4aq. Loses 3 atoms of water at 130°.—According to Millon & Commaille, phosphoric and sulphuric acids may also combine with casein both together. See Mulder's statement (*infra*).

Hydrochlorate of Casein. Cas, HCl.

Nitrate of Casein. Cas, NO^5 + 8aq. Loses 6 atoms of water at 115°, 7 atoms at 130°, and 8 atoms at 160°.

Arseniate of Casein. Cas, AsO^5 + 8aq. Loses the whole of the water at 130°.

Chromate of Casein. Cas, CrO^3 + 8aq.

Oxalate of Casein. Cas, C^2O^3 + 5aq. Loses 3 atoms of water at 115°, 4 atoms at 130°, and 5 atoms at 150°.

Milk is not precipitated by dilute solution of *boracic acid*, but on adding small quantities of milk to strong solutions of the acid, casein is separated in flocks, which may be freed from fat and other impurities by washing with aqueous boracic acid, water, and ether. When chloride of sodium is previously added to the milk, no albumin is thrown down with the casein (Brücke, *Wien. Acad. Ber.* 2 Abth. 55, 881; *Chem. Centr.* 1867, 1006).

The behaviour of milk with carbonic acid varies according to the length of time it has been kept. *a.* Perfectly fresh milk is not precipitated by a current of carbonic acid and subsequent boiling. *b.* A few hours later, the milk coagulates on boiling if carbonic acid has been previously passed into it. *c.* After a further lapse of a few hours, it coagulates on boiling, even without carbonic acid. *d.* Still older milk coagulates when treated with carbonic acid without boiling. *e.* Lastly, it coagulates spontaneously (Hoppe-Seyler).

The precipitates produced by *sulphuric*, *hydrochloric*, and *nitric acids* in aqueous casein (-soda), or in milk, are insoluble in excess of the acids, but when excess of acid is removed by repeated washing with water, the resulting neutral compound is soluble in warm water (Berzelius). The casein thrown down by sulphuric acid contains 2·89 p. c. SO^3 and 1·83 PO^5 (Mulder). Subsequently (*J. pr. Chem.* 44, 489) Mulder stated that sulphate of casein contains 8·45 p. c. SO^3. The precipitated casein loses the whole of the sulphuric acid when washed (Rochleder).

Casein dissolves in water containing hydrochloric acid (Hoppe-Seyler). This solution exhibits the reactions of Bouchardat's albuminose (p. 268), (Bouchardat, *Ann. Pharm.* 43, 124). The precipitate thrown down by *hydrochloric acid* from casein-potash dissolves in a somewhat larger quantity of the acid and is re-precipitated by a much larger quantity (Braconnot). When hydrochloric acid is added to diluted milk till a bulky coagulum and a clear yellowish liquid are formed, and the former is washed with water containing 2 p. c. of hydrochloric acid, the precipitate thus obtained swells up in pure water as the hydrochloric acid is removed, ultimately becoming gelatinous, and then dissolving in water at 40°. This solution contains hydrochloric acid; it is precipitated by acids and by alkalis. The precipitate thrown down by hydrochloric acid dissolves in alcohol, forming a solution from which ether throws down dense flocks, which contain hydrochloric acid

[2·61 p. c. (Schlossberger), and swell up and dissolve in water. The flocks dry up to a brittle, friable, gummy mass (Bopp; Schlossberger)]. On dialysing the solution of hydrochlorate of casein, a liquid is obtained which is coagulated by heat, by mineral acids, and by acetic acid (Schützenberger, *Par. Soc. Bull.* 1, 285).

Acetic acid, in small quantity, throws down from casein-potash a flocculent curdy precipitate, which dissolves in excess of the acid (Berzelius; Schüber). The precipitate is free from acetic acid (Mulder; Rochleder).

Casein heated with *glacial acetic acid* to 180° in sealed tubes, yields hydrosulphuric acid and tyrosine (Lubarin, *Med. Chem. Unters.* 1871, 463).

Hydrocyanic and *tannic acids* do not precipitate alkaline casein. *Citric* and *tartaric acids* in excess readily dissolve the precipitate formed at first (Millon & Commaille). According to older statements, liquids containing tannic acid coagulate milk.

Since milk when exposed to the air, generates a large quantity of acid, the casein it contains is then thrown down as a coherent mass; *sour cheese*, *cream cheese*. In the course of milk turning sour three periods are to be distinguished:—*a*. The milk is liquid, and deposits albumin-like flocks on boiling. *b*. It is liquid, but curdles on boiling. *c*. It is curdled. These various conditions are determined by the amount of lactic acid formed (Scherer). See also above the behaviour of milk with carbonic acid.

With Bases. — Casein dissolves easily in aqueous ammonia, and in fixed alkalis and their carbonates.

Its solution in aqueous *ammonia* is not precipitated by alcohol (Millon & Commaille). The casein thrown down by alcohol from milk swells up to a jelly in cold aqueous ammonia, and dissolves in presence of more water (Soubeiran).

Casein-potash and *Casein-soda.* — Casein dissolves much more readily than egg- or milk-albumin in *alkaline* water (Millon & Commaille). It neutralises *carbonate of soda*, but does not expel carbonic acid from bicarbonate of potash in the cold (Rochleder). — On heating 5 pounds of fresh curds to 100°; washing with water; dissolving in water with the help of 12·5 grammes of bicarbonate of potash; evaporating the solution; dissolving the residue in boiling water; removing the butter; precipitating with sulphuric acid; washing the precipitate and dissolving it in a very small quantity of potash-ley; mixing the solution with at most an equal volume of alcohol; and allowing it to stand for 24 hours,—sulphate of potash and butter separate, whilst the filtrate, on evaporation, yields casein containing potash. Casein-potash is thus obtained as an amorphous mass, which resembles gum-arabic; reddens litmus; dissolves to a clear, thick, viscid liquid in cold and in boiling water; and forms perfectly soluble pellicles when its aqueous solution is evaporated (Braconnot).

An aqueous solution of casein (-soda) boiled in an open vessel, does not coagulate in a mass, like solution of albumin, but becomes covered with a pellicle which is nearly insoluble in water (Berzelius). Milk pellicles are formed even when oxygen is excluded by a current of carbonic acid (Hoppe-Seyler). Contrary to the statements of Scherer (*Ann. Pharm.* 40, 1). See above his analysis of the pellicle of milk.

Aqueous solutions of casein-potash are precipitated by a large quantity of potash- or soda-ley, the precipitates dissolving when washed with water (Braconnot).

Casein-potash dissolves in very weak spirit (Braconnot). Solutions of casein in potash- or soda-ley are not precipitated by alcohol (Millon & Commaille). When milk is mixed with alcohol till it coagulates, and the curd is boiled with alcohol, it dissolves for the most part, and separates from the solution on cooling in flocks which dissolve in water and boiling alcohol, and leave an alkaline ash when incinerated, whilst the portion of the coagulum insoluble in alcohol leaves a neutral ash (Scherer). Ether free from alcohol does not coagulate aqueous casein (-soda) (Gmelin). — Sugar in large quantity throws down from casein-potash a precipitate soluble in water (Braconnot).

Casein destroys the alkaline reaction of *bisodic phosphate*, and dissolves therein to a frothing, turbid liquid, which leaves a glassy film when evaporated (Rochleder). This solution, like that of casein in soda-ley, when submitted to dialysis, gives up a portion of the salts: the remaining neutral solution of casein is not affected by boiling, but gives curdy precipitates with alcohol and sulphuric acid. The precipitate obtained from the phosphate of soda solution contains 8·3 p. c., that from the solution in soda-ley 5·1 p. c. of the dry substance of ash (A. Müller, *J. pr. Chem.* 103, 49).

When casein precipitated by sulphuric acid is digested with *carbonate of baryta* or *carbonate of lime*, a portion of these bases is dissolved (Berzelius; Gmelin). The carbonates of *lime*, *baryta*, *magnesia*, *cupric oxide*, and *lead-oxide*, as also *binoxide of tin*, form insoluble precipitates when digested with solution of casein-potash (Braconnot). — Small quantities of *lime-water* precipitate milk; larger quantities re-dissolve the precipitate (Scheele). — When casein is agitated with water and baryta, lime, or magnesia, and the liquid is filtered, solutions are obtained, from which alcohol throws down compounds of these bases with casein. The *baryta compound*, $Cas,BaO + 4aq.$, ($Cas = C^{108}N^{14}H^{97}O^{29}$), and the *lime-compound*, $Cas,5CaO + 4aq.$, absorb carbonic acid from the air, which is not the case with the *magnesia-compound*, $Cas,2MgO + 4aq.$ (Millon & Commaille).

A mixture of casein and *phosphate of lime* dissolves very easily in a small quantity of aqueous alkali, forming a faintly alkaline liquid, which behaves like milk when heated with acids and salts (Haidlen, *Ann. Parm.* 45, 267).

Aqueous solutions of all the compounds of casein with bases take up *cupric hydrate*, whereby even the ammonia- and alkali-compounds are rendered precipitable by alcohol. In this way the following bodies are obtained:—

Casein with Ammonia and Cupric oxide, $Cas,NH^4O,3CuO$, a greenish-grey precipitate thrown down by alcohol from the violet-green solution.

Casein with Potash and Cupric oxide, $Cas,6KO,CuO$; and *Casein* with *Soda* and *Cupric oxide*, $Cas,5NaO,2CuO$. The precipitates thrown down by alcohol from the fine violet solutions run together into sticky masses, which, after kneading with alcohol, fall to powder in ether.

Casein with Baryta and Cupric oxide, $Cas,4BaO,3CuO + 7aq.$ *Casein* with *Lime* and *Cupric oxide*, $Cas,6CaO,3CuO$; a fine violet. *Casein* with *Magnesia* and *Cupric oxide*, $Cas,2MgO,CuO$.

Casein with Potash and Zinc-oxide, Cas,7KO,2ZnO. — When precipitated oxide of zinc is triturated with aqueous casein-potash, an elastic mass is formed which produces a thick pulp with water, and afterwards dissolves. After drying it is white and horny: it is not precipitated from solution by alcohol.

Casein with Ammonia and Mercuric oxide. — When casein is triturated with yellow mercuric oxide and ammonia, the mass swells up and becomes paler, and, when washed with ammonia-water, alcohol, and ether, leaves a compound of 1 atom of casein with 2 atoms of mercurammonium oxide containing as much as 38·93 p. c. of mercury.

Casein with Silver-oxide, Cas,AgO, is precipitated by neutral nitrate of silver from ammoniacal solution of casein. The white curdy precipitate dissolves very easily in ammonia, and blackens on exposure to light (Millon & Commaille).

Milk, to which *chloride of sodium* or *saltpetre* has been added, remains fluid for a considerable time, coagulating only after keeping for 7 days: when boiled it forms flocks, not a coagulum (Scherer). Milk coagulates at the boiling heat when saturated with salts of the alkalis or alkaline earths (Scheele). — Casein is insoluble in solution of chloride of sodium (Hoppe-Seyler). It dissolves in solution of chloride of sodium containing 10 p. c. of the salt, but is rendered insoluble therein by heat or by contact with moist air or alcohol (Denis).

The casein of Denis dissolves in water, owing to the presence of *sulphate of magnesia:* the solution deposits flocks of casein when largely diluted with water. — *Gypsum*, digested with solution of casein-potash, throws down an insoluble precipitate (Braconnot).

Milk is curdled by *alum*, *stannous chloride*, *neutral acetate of lead*, and *ferrous sulphate.*

From aqueous *cupric sulphate*, milk throws down a pale, bluish-green precipitate; with excess of milk the filtrate is pale-green. The precipitate dries up to a pale-green, brittle mass containing 3·58 p. c. of cupric oxide. It is resolved by (sulphuric, hydrochloric, or) acetic acid into a white precipitate containing copper, and a colourless solution, in which hydrosulphuric acid produces a brown precipitate, and hydrosulphate of ammonia a brown precipitate soluble in excess of the precipitant. Caustic potash colours the acetic solution violet, without precipitation: it first colours the precipitate violet, and then forms with it a violet solution and white, insoluble flocks. Ammonia colours the precipitate blue; iodide of potassium greenish; ferrocyanide of potassium reddish-brown, without dissolving it. — The green filtrate obtained with cupric sulphate and excess of milk, still contains copper. It gives with potash a yellowish precipitate, which afterwards dissolves to a violet-coloured liquid: ammonia produces a blue solution and a white precipitate; hydrosulphuric acid colours it brown; iodide of potassium neither colours nor precipitates it; ferrocyanide of potassium throws down a reddish-brown, phosphate of soda a white precipitate (C. G. Mitscherlich, *Pogg.* 40, 120).

Milk is coagulated by *mercurous* and *mercuric nitrate. Mercuric chloride* throws down a large quantity of flocks, which make the liquid thick. According to Elsner (*Pogg.* 47, 609) mercuric chloride behaves with casein in the same manner as with albumin; the precipitate produced contains 11·18 p. c. HgO. — *Nitrate of silver* throws down from milk large white flocks, which turn red and then brown on exposure to light.

The *platinum-compound* of casein contains, on the average, 6·53 p. c. of platinum: it sometimes contains a smaller proportion of water than at others. When precipitated from a hot solution, it contains 8·61 p. c. Pt., and 4·5 Cl. (Millon & Commaille). In another place (*J. Pharm. Chim.* [4] 1, 204), Millon & Commaille give the formulæ $Cas,PtCl^2$ (calc. 7·28 p. c. Pt.) and $Cas,HCl + PtCl^2$ (calc. 7·16 p. c. Pt.). — When sulphate of casein is dissolved in a large quantity of hydrochloric acid, chloride of platinum throws down from the solution a precipitate represented by the formula $Cas,SO^3,HCl,PtCl^2 + 4aq.$ (Millon & Commaille).

Casein with Platinum-cyanide. — Platinocyanide of potassium behaves with solutions of casein as with egg-albumin (p. 300), but the precipitate, which is gelatinous at first, collects together in the middle of the vessel. The compound burns with difficulty, leaving 11·26 p. c. of platinum, or twice as much as the corresponding albumin-compound (Schwarzenbach, *Ann. Pharm.* 133, 193). Diakanow (*Tubing. medic. chem. Untersuch.* 1867, 1, 231) and A. Fuchs (*Ann. Pharm.* 151, 372) found the precipitate thrown down by platinocyanide of potassium from acetate of casein to contain varying proportions of platinum: after washing the precipitate with water till the acid reaction disappears, it dries up to a dense mass, from which some solution of platinum-salt exudes, and it then contains 4·73 to 4·82 p. c. of platinum (Diakanow). Fuchs found 1·49 to 4·92 p. c. of platinum in the precipitate dried at 100°.

Strong *acetic acid* renders dried casein translucent, and causes it to swell, without dissolving it (Lieberkuhn). — Casein, precipitated by acids, dissolves in warm aqueous *acetate of potash* and *soda* (Braconnot).

Milk is incompletely precipitated in small flocks by *alcohol:* from the precipitate collected on a filter, water takes up a large quantity of casein (Gmelin). — Milk is coagulated at the boiling-heat on saturating it with sugar or gum (Scheele).

Galactin. — Besides casein and albumin, milk contains a gelatinous substance which may be detected after the diffusion of the milk through membranes. It occurs in the mother-liquor of milk-sugar, and causes it to gelatinise on addition of alcohol. It was thus obtained by Fourcroy & Vauquelin, and described by them (where?) as precipitable by tannic acid and chlorine, but not by acids (Morin, *N. J. Pharm.* 25, 423; *J. pr. Chem.* 62, 509). According to Corvisart (*Compt. rend.* 35, 244), the same substance occurs in the white of hens' eggs.

Lactoprotein. — Occurs, according to Millon & Commaille, to the extent of 0·3 to 0·35 p. c. in cow's milk, and is obtained in combination with mercuric oxide by dropping acetic acid into milk diluted with 4 times its volume of water (5 or 6 drops of 10 p. c. acetic acid to 20 p. c. of milk) to free it from casein and fat, boiling to get rid of albumin, and precipitating the filtrate with mercuric nitrate, not in excess. The precipitate thus formed contains equal numbers of atoms of lactoprotein, $C^{36}N^5H^{31}O^{18}$, and mercuric oxide: it is white and amorphous, turns red on boiling, and is yellow or red when dry. It is insoluble in water, alcohol, and ether, but dissolves in excess of the precipitant and in nitric acid. Lactoprotein is likewise precipitated by mercuric sulphate, but not by mercuric chloride: hydrosulphuric acid decomposes this precipitate, at the same time altering the lactoprotein (Millon & Commaille, *N. J. Pharm.* 46, 273 and 358; *Kopp's Jahresber.* 1864, 622). Commaille afterwards (*Chem. Centr.* 1867, 588) described lactoprotein as very similar to synaptase, acting as a ferment in milk. According to Hoppe-Seyler (*Analyt. Zeitschr.* 3, 427) lactoprotein is casein or albumin, or at any rate a mixture containing both these bodies.

Fibrin.

HATSCHETT. *Scher. J.* 6, 308.—FOURCROY & VAUQUELIN. *N. Gehl.* 2, 243.—BERZELIUS. *Schw.* 9, 377.—*Scher. Ann.* 8, 256; *Lehrb.* 3, Aufl. 9, 50.
FERD. MICHAELIS. *Schw.* 54, 94.
J. VOGEL. *Ann. Pharm.* 30, 29; *Berzel. Jahresber.* 20, 549.
MULDER. *Pogg.* 40, 255.—*Ann. Pharm.* 47, 300.
SCHERER. *Ann. Pharm.* 40, 1.
DUMAS & CAHOURS. *N. Ann. Chim. Phys.* 6, 437.
BOUCHARDAT. *Compt. rend.* 14, 962; *Ann. Pharm.* 43, 120; *Berzel. Jahresber.* 23, 593.
LIEBIG. *Ann. Pharm.* 57, 129; 73, 125.
MELZENS. *N. Ann. Chim. Phys.* 33, 170; *Kopp's Jahresber.* 1851, 576.

See further the literature referred to under Paraglobin, p. 271.

Blood fibrin. Faserstoff

Blood drawn from the animal body coagulates in a few minutes, from separation of fibrin. Fibrin likewise separates from blood freed from corpuscles, on standing or whipping.

For the older investigations and views with regard to this phenomenon, see *Handbuch.* viii, 154 *et seq.*; Lehmann's *Physiol. Chemistry*, ii, 195, *et seq.* Since that time Brücke, Denis, Al. Schmidt, and Eichwald, have put forward the following views on the separation of fibrin:—

1. Denis supposes blood to contain a substance, called plasmin, convertible into fibrin. In the process of coagulation this body is resolved, one-third into solid fibrin, and two-thirds into soluble fibrin.

2. Al. Schmidt distinguishes a fibrinoplastic and a fibrinogenous substance, by the reciprocal action of which fibrin is produced. Both these bodies occur in animal fluids, not always in the proportions in which they form fibrin, some fibrinoplastic substance remaining in solution in serum after the separation of fibrin, whilst transudations, the fluid of hydrocele, and of the pericardium, lymph, and chyle, contain exclusively or chiefly fibrinogenous substance.

3. Brücke and Eichwald contend, in opposition to Al. Schmidt, that his fibrinoplastic and fibrinogenous substances differ neither from one another nor from paraglobin, and that it is impossible, or at least difficult, to obtain fibrin by mixing artificial solutions of the two sub-

stances. Whilst, however, Brücke considers blood to contain only one albuminous substance in solution, viz., serum albumin, and, consequently, regards fibrin as identical with coagulated serum albumin, Eichwald distinguishes from paraglobin and syntonin a third constituent of blood, viz., soluble fibrin. According to Brücke (*Virch. Arch.* 12, 81 and 172) blood coagulates because it is withdrawn from the influence of the walls of the living vessels which kept it fluid by virtue of a peculiar action. Coagulation is probably brought about by lime- and magnesia-salts, the bases of which go down with the fibrin in quantity larger than that which corresponds to the phosphoric acid precipitated at the same time. On mixing plasma with an equal volume of water containing acetic acid, neutralising incompletely with ammonia, and warming, a quantity of coagulable serum albumin is thrown down, equal to the fibrin formed by agitation *plus* the serum albumin separable from the serum. Fibrin is said to be formed, therefore, at the expense of a part of the serum albumin, just as, on the other hand, albumin may be converted into fibrin (*Pseudofibrin*, p. 304). Afterwards (*Chem. Centr.* 1867, 999) Brücke assumed the existence of a "true fibrinoplastic substance," forming a constituent of Schmidt's fibrinoplastic substance [and acting apparently, as a ferment, somewhat after the manner of pepsin (Kr.)].

4. According to Eichwald, the formation of solid fibrin results from the withdrawal of alkali from soluble fibrin. The alkalinity of blood decreases rapidly after it is drawn from the body, till coagulation takes place. When coagulation takes place by exposure to air, the air first gives carbonic acid to the alkali of the serum, and, secondly, oxygen to the red corpuscles, which are then brought into a favourable condition for forming carbonic acid. For the same reasons air promotes the separation of fibrin from slowly coagulating transudations (Eichwald).

The *plasmin* of Denis is obtained as follows:—Venous blood is drawn into $\frac{1}{7}$th its volume of a saturated solution of sulphate of soda; the blood corpuscles are allowed to settle; the liquid is filtered; and the filtrate is saturated with chloride of sodium, which precipitates the plasmin. It is to be washed with saturated solution of chloride of sodium, but cannot be freed from adhering chloride of sodium.

Plasmin is a soft white mass, which may be dried below 40°, but undergoes alteration immediately if the chloride of sodium be removed. It dissolves in water, probably only on account of the presence of chloride of sodium, to a limpid liquid, precipitable by acids and alkalis, and coagulable by heat and by alcohol. On standing for five minutes, or longer, the solution deposits solid, colourless, and transparent fibrin, which is not attacked by non-saturated solutions of chloride of sodium.

The portion of the plasmin remaining in solution after this formation of fibrin is Denis's *soluble fibrin*. The liquid in which it is dissolved is partially precipitated by boiling, and more abundantly by alcohol. The latter precipitate dissolves in a large quantity of 10 p.c. solution of chloride of sodium. It dissolves when the liquid mixed with alcohol is heated to boiling, and re-appears in part on cooling. Most acids, and also powdered sulphate of magnesia, throw down from the liquid precipitates soluble in water. This non-coagulable soluble fibrin possesses, therefore, the properties of fibrin dissolved in a non-saturated solution of chloride of sodium (Denis).

According to Denis solid fibrin is either pure or modified fibrin.

a. *Modified Fibrin.* Fibrin formed from arterial blood, spontaneously or by whipping, or deposited from a solution in sulphate of soda on dilution, is insoluble in non-saturated solution of chloride of sodium, and does not swell in it. Fibrin which has been heated to 100° behaves in the same way.

b. *Pure Fibrin.* Fibrin obtained from venous blood by whipping dissolves easily, after washing, in dilute warm hydrochloric, phosphoric, and acetic acids, and in warm aqueous alkalis and neutral salts. It dissolves in 3 parts of a 10 p.c. solution of chloride of sodium at 40° to 50° in two hours, and at the ordinary temperature in twenty-four hours. The moist substance dissolves also when triturated to a pulp with one-third of its weight of chloride of sodium mixed with two or three parts of water, and heated to 40° or 50°. These saline solutions are precipitated by a large quantity of water, the precipitate re-dissolving in solution of salt; they coagulate at 60° to 65°. On heating them to 100°, the water takes up an albuminous substance resulting from the decomposition of the fibrin. Saline solutions of fibrin are precipitated also (1) by acids, when not very dilute, the precipitate disappearing on addition of water or of a larger quantity of acid; (2), by alcohol: the fresh precipitate dissolves completely in solution of salt, but not after standing some time in contact with alcohol; (3), by powdered sulphate of magnesia: the precipitate dissolves, after draining, in a small quantity of water, the solution depositing fibrin again on addition of more water. See further Denis (*Compt. rend.* 47, 996; 52, 1239).

Eichwald regards Denis's plasmin as a mixture containing paraglobin, together with the peculiar fibrin-forming substance, soluble fibrin.

Eichwald's *soluble fibrin* is obtained by the following process, which must be conducted quickly, without access of air, and near 0°. Horse's blood is allowed to flow from the veins into $\frac{1}{5}$th of its volume of a saturated solution of sulphate of soda. After standing for 6 to 9 hours the yellow transparent plasma is siphoned off and filtered, and the filtrate is mixed with an equal volume of saturated solution of chloride of sodium. The dirty-grey turbid precipitate first produced quickly collects into large, coherent, loose, white masses, which are washed with a one-third saturated solution of chloride of sodium till the filtrate is no longer precipitated by ferrocyanide of potassium and acetic acid.

The precipitate thus obtained contains alkali in combination, and, in consequence, dissolves slowly in water, forming a solution which speedily coagulates from formation of fibrin. When agitated in closed vessels with water to which soda has been added to distinctly alkaline reaction, and left to stand for two hours, it gradually swells up and dissolves completely to a grey and turbid liquid, which becomes colourless and transparent when diluted.

This solution is not precipitated by boiling. When a current of carbonic acid is passed into it, it becomes turbid from separation of flocks, fibres, or membranes. It is so completely precipitated, in white floating masses, by an equal volume of a saturated solution of chloride of sodium, that the filtrate is not rendered turbid by ferrocyanide of potassium and acetic acid. This precipitation takes place even in strongly alkaline solution, and is partially prevented only by a large excess of soda. On cautiously adding dilute acetic acid to the solution, it deposits flocks which in a few minutes combine to form fibrin. Excess of acetic acid re-dissolves the flocks completely, whereupon ferrocyanide of potassium and chloride of sodium throw down precipitates (Eichwald).

On Schmidt's fibrinoplastic substance, see Paraglobin (p. 271). His *fibrinogenous substance* is obtained as follows:—

Some liquid containing both these fibrin-forming substances (the diluted plasma of horse's blood, for instance) is first freed from fibrinoplasmin by a current of carbonic acid. The fibrinogen may then be precipitated from the filtrate in flocks, by concentrating it in a vacuum, dropping in alcohol till turbidity is produced, and setting aside for some hours. It must be remembered that, inasmuch as alcohol promotes the formation of fibrin, the precipitate may, under certain circumstances consist of fibrin, and, moreover, that too much alcohol precipitates also serum albumin. The latter applies more particularly to the use of transudations.

The fibrinogenous, like the fibrinoplastic substance, is precipitated by a current of carbonic acid, but much less rapidly and easily, so that the mode of preparation described under fibrinoplasmin may likewise be adopted for the preparation of fibrinogen from transudations. A further consequence of this behaviour of the two substances is that the precipitate produced by carbonic acid in diluted blood-plasma contains also fibrinogen, and therefore coagulates in the course of a few hours from very faintly alkaline solutions.

Fibrinogen thrown down by alcohol forms a finely granular, readily coherent precipitate, which dissolves somewhat less easily than fibrinoplasmin in alkaline water, but otherwise dissolves and reacts like fibrinoplasmin.—It decomposes peroxide of hydrogen in neutral or slightly acid solution very rapidly, the action ceasing however at 72° (Gianuzzi).

The two fibrin-forming substances are, therefore, characterized chiefly by their action upon each other. Whilst neither the fibrinoplastic nor the fibrinogenous substance in slightly alkaline solution, deposits fibrin on standing, the formation of fibrin takes place, with liberation of alkali, on mixing the solutions. In performing this experiment it is best to employ an artificially formed solution of one, and a natural solution of the other of these substances, as, for instance, blood-serum containing fibrinoplasmin, and fibrinogen dissolved in alkaline water,—or, conversely, transudations containing fibrinogen, and artificially dissolved fibrinoplasmin. The coagulation seldom takes place with solutions both of which are artificially prepared. Moreover, solutions otherwise suitable do not coagulate when acid or too strongly alkaline, or when they contain large quantities of neutral salts (Al. Schmidt).

According to Eichwald, pericardial fluids (which, according to Al. Schmidt, contain little or no fibrinoplastic substance) invariably deposit fibrin on standing. This deposition is accelerated by a current of carbonic acid, or by partially neutralising the strong alkaline liquid with phosphoric, hydrochloric, or acetic acid. On diluting pericardial fluid—previously freed from fibrin by passing carbonic acid into it and [illegible]-with 10 to 20 times its volume of water, and again treating it with carbonic acid, paraglobin is thrown down. The filtrate still contains syntonin precipitable by acetic acid. The pericardial fluid therefore likewise contains paraglobin in solution after the separation of fibrin: hence it does not differ from blood-plasma in containing less fibrinoplastic substance, but contains the same albuminous substances, and coagulates more slowly on account of the greater amount of alkali present. If paraglobin added to the pericardial fluid causes a deposition of fibrin, it is not because of the reciprocal action of fibrinoplasmin and fibrinogen, but because the alkalinity of the fluid is thereby altered (Eichwald).

According to Smee (*Proc. Roy. Soc.* 12, 399, 505; 13, 350; *Jahresber.* 1863, 617; 1864, 614), fibrin is formed in perfectly defibrinated blood serum by contact with oxygen at 36°, or by electrolysis. It is likewise formed, under the same circumstances, in egg albumin acidified with a little acetic acid, and in gastric juice mixed with albumin or glutin. See Melsen's observations on the solidification of albumin (p. 284).

According to Bouchardat (*Compt. rend.* 14, 962; *Ann. Pharm.* 43, 120), fibrin is made up of the following three substances in varying proportions:—*a.* Albuminose, which is identical with uncoagulated albumin. *b.* Gelatin. *c.* Epidermose. The two latter substances form together a tissue which encloses the albuminose. Leconte and Goumoens suppose fibrin to contain two different constituents. (See p. 254). — According to Béchamp & Estor (*Compt. rend.* 68, 408; *Par. Soc. Bull.* 11, 505), fibrin is a pseudomembrane formed by the microzyma of the blood and its secretions.

Preparation. Fibrin is separated from fresh blood by whipping, and purified by washing with water till all colouring matter is removed, and afterwards freed from fat by treatment with alcohol and ether. Melsens, after treating the fibrin with water for some hours, washes it for several hours or a day with water containing carbonic acid, then with water acidulated with acetic acid, which causes it to swell up, and lastly with pure water. In this way the reddened or lumpy portions are got rid of, and the fibres broken up.

Or, blood-clot is cut into as thin shavings as possible, which are to be soaked in water so long as they give up colouring matter thereto in the course of a few hours.

Fibrin is deposited from plasma, on standing, in the form of a transparent jelly, which when detached from the walls of the vessel, cut up, and washed, becomes converted into stringy fibrin.

Properties. Fibrin in the moist state forms an elastic, glossy, white, opaque [translucent (Melsens)], fibrous mass, which becomes hard and friable when dried. It is inodorous and tasteless.

	Mulder.	Vogel.	Scherer.			
	Dried at 100°.		*Dried at* 100°.			
			a.	*b.*	*c.*	*d.*
C	53·81	53·11	54·45	54·00	54·15	54·15
H	15·54	18·12	15·79	15·72	16·01	
N	6·91	7·29	7·10	6·84	7·22	6·96
O and S	23·41	21·48	22·66	23·44	22·62	
Ash		2·66	1·3	1·37	2·3	

	Dumas & Cahours. Dried at 140°. a.	Dumas & Cahours. Dried at 140°. b.	Verdeil. at 100°.	Verdeil. at 140°.
C	52·69	52·78	50·88	52·13
H	16·59	16·78		
N	7·00	6·96	7·09	7·07
O and S	23·72	23·48		
Ash	1·95	1·54	2·1	

Remarks on the analyses. Mulder's fibrin contained also 0·33 p.c. of phosphorus. — Scherer analysed (*a*) venous fibrin; (*b*) the same, dissolved with the help of saltpetre and potash and precipitated by alcohol: (*c*) fibrin precipitated from a solution in acetic acid by carbonate of potash; (*d*) precipitated from an alkaline solution by acetic acid. — Dumas & Cahours examined fibrin (*a*) from ox blood, (*b*) from human blood, and also that from the blood of the sheep, calf, horse, and dog, with the same results.

Melsen's (*Compt. rend.* 20, 1438) found 17·7 p.c. of nitrogen on the average. The amount of sulphur was found by Mulder to be 0·63, afterwards 1·2 p.c.; by Ruling (*Ann. Pharm.* 58, 311), 1·23 to 1·45 p.c.; by Verdeil (*Ann. Pharm.* 58, 317), 1·60 p.c. — Fibrin cannot be obtained free from iron, and still contains it, even when the ash appears white (Liebig).

Decompositions and Combinations. 1. Moist fibrin absorbs *oxygen* and evolves carbonic acid (Scherer). When diffused through water either pure or alkaline it is not attacked by ozone (Gorup-Besanez, *Ann. Pharm.* 110, 101). — 2. When oxidised with *binoxide of manganese* and *sulphuric acid*, or with *bichromate of potash* and *sulphuric acid*, it yields the same products as casein (p. 311), but an especially large quantity of butyric acid and butyral are formed (Guckelberger, *Ann. Pharm.* 64, 39).

3. Dried fibrin swells up in *water*, turns soft and flexible, and trebles its weight from absorption of water. When pressed it again becomes hard and nearly dry (Berzelius). When *heated with water* to 72°, or with other neutral liquids, or when kept for some time under alcohol, fibrin becomes similar to coagulated albumin; it shrinks and becomes less extensible, and is then no longer soluble in salts and dilute acids, but still soluble in alkalis.

Fibrin boiled with water for a quarter of an hour yields only a trace of soluble substance (Mulder), but on prolonged boiling it undergoes a change, part being dissolved. The undissolved portion possesses the properties of fibrin at first, but after repeated boiling it loses its solubility in ammonia and acetic acid (Berzelius; Berthollet, *N. Gehl.* 5, 318).

When fibrin is boiled with water for forty hours, 20·67 p.c. of it is dissolved, and of this, 40·7 p.c. is soluble in alcohol, the remainder in water only (Mulder). The dissolved portion tastes like broth, and when dried is pale-yellow, hard, and brittle (Berzelius). It resembles gelatin altered by long boiling (Mulder). When fibrin is boiled with 3 or 4 parts of water till the bulk of the liquid is reduced to one-half, and strained, the strained liquid (more especially when fibrin of the buffy coat of blood is employed) solidifies to a jelly, which is precipitated by chlorine, mercuric chloride, and tannic acid, but not by nitric acid, and hence possesses the properties of gelatin (Bouchardat). — Dumas & Cahours obtained no jelly. The liquid was precipitated by mercuric chloride and tannic acid, and, when concentrated, also by nitric acid. It was coloured blue by hydrochloric acid, and precipitated by alcohol only when concentrated. The dissolved substance exhausted with alcohol contained at 140°, after deducting 11 p.c. of ash, 47·91 p.c. C., 14·96 N., and 6·87 H., and therefore differs from gelatin in composition. The undissolved portion of the fibrin contains 53·49 p.c. C., 15·88 N. [19·5 p.c. N. (Melsens, *Compt. rend.* 20, 1438)], and 7·09 H. (Dumas & Cahours).

Fibrin, *boiled with water* at 100° to 120° *in a Papin's digester*, dissolves almost entirely in a few hours. The solution is precipitated by hydrochloric acid, alum, mercurous nitrate, and tannic acid, but not by neutral or basic acetate of lead, or by alcohol. It dries up to a transparent, brittle, gummy mass, which re-dissolves in water, and assumes a fine lilac colour with excess of hydrochloric acid (Vogel). Similar observations were made by Wöhler (*Ann. Pharm.* 41, 238). Mulder, by boiling fibrin for four hours, or longer, in a Papin's digester, obtained an undissolved portion containing 53·07 p.c. C., 6·91 H., and 14·82 to 15·63 N. The dissolved portion, purified by treatment with alcohol, contained 50·97 p.c. C., 6·62 H., and 15·38 N., and was partially precipitated by neutral acetate of lead, but not completely, even after addition of ammonia. According to Mulder, the dissolved portion is protein-trioxide, the undissolved portion protein-bioxide.

W. Schmid (*Anal. Zeitschr.* 8, 131) has made the following observations: *a.* Fibrin treated with alcohol and afterwards heated to 150° with water for five hours, evolved gas, swelled up, and yielded an acid solution which was not precipitable by acetic acid, but precipitable by nitric acid, neutral acetate of lead, cupric sulphate, mercuric chloride, tannic acid, ferrocyanide of potassium and acetic acid, and alcohol. — *b.* On heating fresh fibrin to 150° with water for 16 hours, the solution obtained was precipitable also by acetic acid, and contained ammonia-salts. — *c.* After heating for 36 hours, the solution was still precipitable by acetic acid, and yielded flocks with carbonic acid. All the solutions give the reactions of proteides with Millon's mercury-solution and with potassio-cupric tartrate; none of them contain leucine, tyrosine, or peptone. See p. 257.

4. Fibrin in the moist state rapidly evolves oxygen from *peroxide of hydrogen*, but not after boiling or after digestion with alcohol (Scherer; Thénard, ii, 77). The decomposition takes place only at temperatures below 66° to 72° (Giannuzzi, *Virchow's Arch.* 34, 443). — 5. Fibrin dissolves in *chlorine-water* on prolonged digestion, and afterwards deposits a white powder (Vogel). Chlorine passed into ammoniacal fibrin throws down white flocks of proteinchlorous acid (p. 267) (Mulder).

6. Dry fibrin swells up to a yellow jelly in *oil of vitriol*, without dissolving. The jelly shrinks in water and is insoluble in warm dilute sulphuric acid, but gives up thereto a substance precipitable by infusion of galls. The same shrunken mass is formed when moist fibrin is immersed in dilute sulphuric acid; when washed with water, it is converted into a transparent jelly, which afterwards dissolves. The addition of sulphuric acid again causes the jelly to contract, and precipitates the aqueous solution (Berzelius). — Fibrin submitted to prolonged boiling with moderately dilute sulphuric acid yields the same products as albumin or casein (Bopp). — 7. Freshly ignited *phosphoric acid* behaves in the same way as sulphuric acid; in ordinary phosphoric acid fibrin swells up to a jelly which dissolves in water, form-

ing a solution which is not precipitated by excess of phosphoric acid (Berzelius).

On digesting 6 grammes of fibrin with a mixture of 20 grammes of water and 0·2 gramme of phosphoric acid of sp. gr. 1·845 at the temperature of 40° to 45° for 12 hours, the fibrin swells slightly; the acid liquid is not precipitated by boiling, but gives a permanent precipitate with nitric acid in not too small quantity, and is precipitated also by alcohol and by tannic acid. Acid phosphate of lime behaves in a similar manner (Guibourt).

8. *Nitric acid* colours fibrin yellow and forms products similar to those formed by sulphuric acid. On digestion, xanthoproteic acid is produced.

9. Dry fibrin swells up in fuming *hydrochloric acid* to a jelly, which gradually dissolves to a fine dark-blue liquid (Berzelius). 100 parts of dry fibrin take up at 15°, 7·16 parts of hydrochloric acid gas (Mulder). Prolonged boiling with the fuming acid generates the same products as with albumin and casein (Bopp).

In hydrochloric acid containing $\frac{1}{1000}$ to $\frac{5}{1000}$ of the acid, fibrin swells up to a glassy transparent mass, without dissolving. This mass shrinks to its original bulk and becomes opaque again when immersed in stronger acid (Liebig), or when washed free from acid with water, or neutralised; also on the addition of salts. The fibrin dissolves as syntonin, with the exception of a slight residue, on standing for a day at 20°, or in a few hours at 40°, and rapidly at 60° (Kühne). The undissolved portion is Bouchardat's epidermose; the solution contains his albuminose and gelatin (Bouchardat).

According to Guibourt (*J. Pharm. Chim.* [4] 2, 94) aqueous hydrochloric acid containing $\frac{1}{2000}$th of the acid appears to be best adapted for the solution of fibrin, 100 grammes of acid of this strength almost completely dissolving 4 grammes of most fibrin in 12 hours, at the temperature of 40° to 45°. In other experiments of the same duration and at the same temperature, acid containing $\frac{3}{10000}$ths and $\frac{2}{10000}$ths caused little or no swelling of the fibrin; acid containing $\frac{24}{10000}$ths produced decomposition and partial solution; whilst in acid of 1·2 p. c. the fibrin contracted without dissolving. In the solutions thus formed nitric acid produced abundant white precipitates; only those liquids formed by imperfect swelling up of the fibrin became turbid on addition of alcohol or on boiling.

The hydrochloric acid solution gives with carbonate of ammonia a precipitate which, after treatment with alcohol, contains 52·92 p. c. C., 6·81 H., and 15·88 N. (Mulder & Baumhauer). According to Mulder, this precipitate is protein-binoxide. But air takes no part in the solution of fibrin by hydrochloric acid; moreover, the so-called protein-binoxide contains sulphur and phosphate of lime (Liebig).

Chloride of sodium, sulphate of soda, and nitrate of potash throw down from the solution of fibrin in hydrochloric acid a coagulum which, after washing with saturated solution of chloride of sodium, contains the sulphur and phosphate of lime of the fibrin (Liebig).

Fibrin dissolves more rapidly in a mixture of water, hydrochloric acid, phosphoric acid, and phosphate of lime, than in dilute hydrochloric acid (Brücke, *Wien. Acad. Ber.* 43 [2], 619).

10. Strong *acetic acid* converts fibrin into a colourless jelly which dissolves easily in warm water. The solution when evaporated becomes covered with a pellicle and afterwards gelatinises: when the evaporation is continued to dryness, the fibrin is left nearly free from acetic acid, opaque, and insoluble in water either cold or warm. Other acids

throw down from the acetic solution compounds of fibrin with the acids (Berzelius).

Acetic, *citric*, and *tartaric acids* act less powerfully upon fibrin at 40° to 45°, in twelve hours, than hydrochloric and lactic acids; only solutions containing at least 1 p. c. of these acids caused any considerable swelling up of the fibrin, a substance precipitable by nitric acid being then dissolved. In a solution of *lactic acid* containing 0·066 to 6·6 p. c., under similar circumstances, fibrin swells up to a jelly which yields by filtration a liquid precipitable by nitric acid but not by boiling or by alcohol (Guibourt).

11. When fibrin is digested for a few days in a mixture of 1·3 grammes of *hydrochloric acid* with a litre of water (whereby it is rendered gelatinous without being dissolved) (see above), and *yeast* is added, it dissolves completely in 24 hours at 15°, or in 4 or 5 hours at 30° to 40°, forming a colourless liquid which gives flocculent precipitates with acids and alum, is not coagulated by heat, and when evaporated in a vacuum, leaves a pale-yellow residue soluble in warm water (Dumas, *Berzel. Jahresber.* 25, 872). See below the action of pepsin.

12. Moist fibrin soon begins to *putrefy* in moist air, and becomes fluid in a week (Wurtz): under water it loses its coherence and dissolves, in the course of three weeks, to a nearly colourless liquid containing flocks of sulphide of iron. In the decomposition, volatile, badly-smelling products are evolved, together with a little hydrogen. The residual liquid coagulates like albumin when heated, a small quantity of nitrogenous substance remaining in solution (Liebig). The products of putrefaction are the same as in the case of albumin (p. 287) (Bopp).

The albuminous substance thrown down by heat contains, when dried at 130°, 53·9 p. c. C., 15·58 N., 6·99 H., 1·52 S., and 0·28 ash (Liebig). It may be isolated by means of basic acetate of lead and carbonic acid, like egg albumin (Wurtz). On prolonged putrefaction it becomes casein-like, so that an ammoniacal solution, when neutralised with acetic acid and freed from albumin by boiling, gives a second precipitate on further addition of acetic acid. This casein dissolves in excess of acetic acid; it is not precipitated by boiling with chloride of calcium or sulphate of magnesia; it is coagulated by rennet only after addition of milk-sugar, and does not form a casein-pellicle when evaporated (Gunning, *J. pr. Chem.* 67, 52; *Kopp's Jahresber.* 1856, 694).

The putrefaction of moist fibrin is not attended with formation of fat (Gay-Lussac, *Ann. Chim. Phys.* 4, 71, Wurtz). The products formed include a large quantity of butyric acid (Wurtz, *N. Ann. Chim. Phys.* 11, 253). — No fat is produced when carbonate of ammonia or chalk is added to putrefying fibrin: the dark-grey stinking pulpy mass contains volatile fatty acids, and a small quantity of solid fatty acid, probably capric (Brendecke, *N. Br. Arch.* 70, 26).

13. Fibrin behaves with aqueous *ammonia* as with potash, but the decomposition and solution take place more slowly: on evaporating the solution, insoluble fibrin remains behind (Berzelius).

14. When fibrin is placed in very dilute *potash-ley*, it is converted into a jelly, which completely fills the liquid, and when digested at 50° to 60° in closed vessels, gradually dissolves to a turbid nearly colourless

iquid, from formation of albuminate of potash.—Fibrin digested in strong potash-ley evolves ammonia: the fibrin precipitated from the solution no longer gelatinises with acetic acid, and does not dissolve therein (Berzelius). Fused hydrate of potash forms with fibrin the same products as with albumin and casein (Bopp).

The alkaline solution may be neutralised by cautiously adding acetic acid so long as the resulting precipitate continues to re-dissolve in the course of a few hours. When evaporated at a gentle heat, it solidifies to a jelly, and then dries up to a pale-yellow transparent mass, which again forms a jelly and dissolves in water. It blackens silver, from formation of sulphide, and when acidulated emits a very transient odour of hydrosulphuric acid, a small quantity of altered fibrin being at the same time precipitated. Alcohol throws down from the alkaline solution a part of the fibrin in combination with potash (Berzelius). The alkaline solution prepared in the cold does not blacken acetate of lead, or evolve hydrosulphuric acid when acidulated, but these effects are produced when the precipitate produced in the solution by acetic acid is boiled with potash-ley (Liebig). On digesting the alkaline solution with freshly precipitated hydrate of bismuth for 6 or 8 hours, a quantity of sulphide of bismuth is formed, the sulphur of which amounts to 0·52 p. c. of the fibrin employed (Fleitmann, *Ann. Pharm.* 66, 380). See also Mulder (*Scheikund. Onderzoek.* 4, 195; *J. pr. Chem.* 44, 489). The precipitate thrown down by acetic acid from the alkaline solution contains the same proportions of carbon, hydrogen, and nitrogen as fibrin (Dumas & Cahours). When the alkaline solution has been left exposed to the air, the precipitate thrown down by acetic acid contains a larger proportion of oxygen (Mulder's oxyprotein, p. 263).

When the alkaline solution of fibrin is mixed with excess of acetic acid, and chloride of ammonium, chloride of sodium, phosphate, sulphate, or acetate of soda, or chloride of calcium is added, a precipitate is produced which dissolves on heating the liquid and reappears as it cools (Panum). See *Acid albumin* (p. 26).

15. When fibrin is heated with *potash-lime* to 160° or 180°, ammonia and other products are evolved: the residue contains a volatile acid, probably butyric (Wurtz, *N. Ann. Chim. Phys.* 11, 253).—*Baryta* and *lime* form soluble compounds with fibrin (Mulder).

16. In aqueous solutions containing 6 to 10 p. c. of *neutral salts*, especially nitrate of potash, chloride of sodium, and sulphate of soda, fibrin swells up to a slimy mass, which becomes homogeneous and susceptible of filtration only after prolonged digestion.

Denis, who first observed this property, gave the following directions (*Ann. Pharm.* 40, 11):—Moist fibrin (150 parts) obtained from venous blood-clot and thoroughly washed, is triturated with 50 parts of nitrate of potash, with gradual addition of 300 parts of water, and lastly of 3 parts of hydrate of potash, and the mixture is left to itself at 35° to 38°. Powdered fibrin from venous blood dissolves without addition of free alkali; fibrin from arterial or mixed blood or from the buffy coat of inflamed blood dissolves only partially or not at all when treated by Denis's method (Scherer). Fibrin from venous ox-blood loses its solubility very rapidly; that of arterial blood is quite insoluble. The fibrin of human blood dissolves most freely; that of pig's blood with especial rapidity (Lehmann, *Physiol. Chemie*, 1, 334).

For the solution of fibrin 24 to 36 hours are necessary at 10°, and 1 to 2 hours at 40° (Kühne). According to Scherer, the solutions are precipitated by water; but according to Lehmann, this is the case only after short digestion with the saline solution, not after prolonged digestion. The solutions coagulate when heated to 60° (Kühne), to about 73° (Lehmann): the coagulum is no longer soluble in salts. They are precipitated by alcohol and by acetic acid, but not by agitation with ether. According to Scherer, the solution of venous fibrin becomes turbid from the surface downwards on standing in the air, but according to Lehmann, only when putrefaction sets in.

Two grains of fibrin dissolve in 24 hours in 1·5 ounces of water saturated with one of the following salts: iodide of potassium, nitrate of potash, acetate of potash, carbonate of soda, carbonate of ammonia, chloride of ammonium, chloride of barium; in 48 hours in aqueous borax or phosphate of soda; in 72 hours in sulphate of potash. The solutions are clear and viscid like white of egg; they coagulate for the most part on boiling, and are partially precipitated by dilution (Zimmermann, *Pharm. Centr.* 1843, 614; *Berzel. Jahresber.* 24, 656).

According to Eichwald, saline solutions take up from fibrin only the enclosed blood-constituents which are coagulable by heat, without dissolving the fibrin itself.

17. An alkaline solution of fibrin neutralised with acetic acid gives with *basic acetate of lead* a precipitate of white flocks which, when dried at 120°, contained on one occasion 30·63 p. c., and another time 12·75 p. c. of oxide of lead. — The solution gives with *ferric sulphate* yellowish-red flocks; with *cupric sulphate* green flocks containing 7·21 p. c. of oxide of copper; with *mercurous nitrate* a white precipitate, quickly turning grey; and with *mercuric chloride* a white precipitate (Mulder).

18. Fibrin takes up nothing from aqueous *cupric sulphate.* A solution of fibrin in potash-ley throws down from cupric sulphate a precipitate of cupric hydrate, which afterwards dissolves with dark-violet colour (Mitscherlich, *Pogg.* 40, 131). See also p. 262.

19. Fibrin contracts in aqueous solution of *mercuric chloride*, becoming dead-white and friable. When removed from the liquid after 15 minutes' immersion, it is not blackened by alkalis, and the solution does not contain free acid, showing that no calomel has been formed. The fibrin gives up mercuric chloride to solution of chloride of sodium (Lassaigne, *Ann. Chim. Phys.* 64, 107).

20. *Nitrate of silver* throws down from acetate of fibrin, in presence of free acid only, precipitates containing from 3·43 to 13·12 p. c. of silver-oxide (Mulder).

21. Fibrin dissolved in hydrochloric acid produces with *ferrocyanide of potassium* a precipitate which leaves on ignition 2·8 p. c. of ferric oxide (Berzelius).

22. A faintly alkaline solution of fibrin is not rendered turbid by *platinocyanide of potassium;* but on acidifying with acetic acid, a precipitate is thrown down, which behaves like that produced in solutions of albumin, except that it turns brown at 100° (Schwarzenbach, *Ann. Pharm.* 133, 185). The precipitate contains 5·56 p. c. of platinum (Schwarzenbach, *Ann. Pharm.* 144, 69).

23. Fibrin is insoluble in *alcohol.* After remaining under alcohol for a year, it is brittle and contains 19·2 p. c. of nitrogen (Mulder).

24. *Tannic acid* combines with moist fibrin immersed in it, forming a hard mass which is not susceptible of putrefaction; it precipitates fibrin from its alkaline and acid solutions (Berzelius).

Crystallin or Globulin.

BERZELIUS. *Lehrbuch*, 3 Aufl. 9, 526.—MULDER. *J. pr. Chem.* 19, 190; *Ann. Pharm.* 33, 261.—RÜLING. *Ann. Pharm.* 58, 313.
LIEBERKÜHN. *Pogg.* 86, 306.
VINTSCHGAU. *Wien. Acad. Ber.* 24, 493.
ALEX. SCHMIDT. *Muller's Arch.* 1862, 440.

The albuminous substance of the crystalline lens.

On triturating the crystalline lens till its structure is broken up, diluting with water, filtering, again triturating the residual membranes with water, and evaporating the solutions, there remains a yellow extract, which may be freed from alkaline lactate, chloride of sodium, and organic admixtures by means of alcohol. The crystallin of Berzelius then remains as a pale-yellow mass, which dissolves in water, and is precipitated by lime-water, oxalate of potash, or infusion of galls. The aqueous solution coagulates when heated, from separation of a granular mass (Berzelius).

Mulder washes and triturates the crystalline lens; exhausts it with water; heats the solution to boiling; dries the mass thereby thrown down; treats it with boiling water and alcohol; and dries at 130°. Crystallin thus obtained is white and friable; it blackens metals after treatment with potash, and contains, after deduction of 0·59 p. c. ash, 54·61 p. c. C., 6·94 H., 16 51 N., and 0·25 S. It swells up in oil of vitriol to a transparent jelly, from which water throws down a powder containing sulphuric acid.

Rüling, who prepared crystallin by heating a mixture of the aqueous extract and alcohol, and treating the curdled mass with boiling alcohol and ether, found in the product dried at 100°, 53·25 p. c. C., 7·20 H., and 1·10 S.; and in that dried at 140°, 54·23 p. c. C., 7·07 H., and 1·23 S.—Scherer (*Ann. Pharm.* 40, 24) who dissolved crystallin in potash-ley, and precipitated with acetic acid, found 54 61 p. c. C., 16·22 N., and 6·94 H.

Lehmann (*Lehrbuch der physiol. Chemie.* 1, 360) prepares soluble crystallin by evaporating the fluid of the crystalline lens below 50°, after first neutralising with acetic acid, and treating the residue with ether and weak spirit. He obtains coagulated crystallin by precipitating with hydrochloric acid, washing with the same acid, dissolving in water, precipitating with carbonate of ammonia, and washing with water, alcohol, and ether. It contains, on the average, 1·227 p. c. of sulphur.

Lehmann's soluble crystallin forms a yellow translucent mass, triturable to a white powder; it swells up in water and gradually dissolves to a slimy liquid. This solution becomes opalescent at 73°, milky at 83°, and at 93° deposits a coagulum which collects into flocks separable by filtration only after addition of neutral salts of the alkalis and boiling. The aqueous solution is not precipitated by acetic acid, nor by ammonia, but is at once rendered turbid when the acetic solution is neutralised by ammonia, or the ammoniacal solution by acetic acid. On heating to 50° the solution mixed with a little acetic acid, and thereby rendered opalescent, it deposits a milky coagulum; a solution rendered clearer by the addition of more acetic acid coagulates at 98°, while a solution containing a large quantity of the acid does not coagulate even on boiling.—An aqueous solution of crystallin into which carbonic acid is passed, deposits the crystallin as a non-crystalline precipitate, which re-dissolves when the liquid is exposed to the air, or when oxygen is passed through it. Crystallin behaves in the same manner as egg albumin towards mineral acids and metallic salts. When precipitated from its aqueous solution by alcohol, it is insoluble in water, but boiling alcohol dissolves a portion [owing to the presence of alkali in the crystallin (Scherer)], which is deposited again on cooling. Aqueous crystallin is not coagulated by ether (Lehmann).

The precipitate thrown down by alcohol of sp. gr. 0·82, from concentrated and filtered solutions of crystallin, exhibits the reactions of serum albumin similarly precipitated. After drying it is only partially soluble in cold water, the residue giving up a further portion to water on prolonged boiling. The fresh or dried precipitate dissolves in warm alcohol of sp. gr. 0·92, but not in alcohol of sp. gr. 0·82.—The temperature at which crystallin coagulates depends upon the strength of the solution and the amount of alkali it contains. Strong solutions begin to show turbidity at 70° to 72°, and congeal to a stiff mass at 75° to 80°. Moderately dilute solutions become milky only on warming, without forming a coagulum, and then run turbid through a filter. Crystallin neutralised with acetic acid becomes turbid at 59°, and coagulates at 66°; with more acetic acid a precipitate is produced at 53°. Hence the differences between crystallin and serum albumin disappear when the two bodies are compared under similar circumstances (Vintschgau).

A solution of the globulin of the crystalline lens acidified with acetic acid solidifies to a stiff white paste on dropping into it *platinocyanide of potassium*. The precipitate, after washing, dries up to a transparent, glassy, brittle, and very hygroscopic mass, containing, when dried at 110°, 5·53 p. c. of platinum (Schwarzenbach, *Ann. Pharm.* 144, 66).

According to Lieberkühn, the crystalline lens contains albuminate of potash. On precipitating the filtered aqueous solution of the crystalline lens with ether-alcohol, exhausting the precipitate with boiling alcohol, and precipitating the filtrate with ether, a precipitate is obtained, which behaves like albuminate of potash, and yields 1·44 p. c. of alkaline ash almost entirely soluble in water (Lieberkühn).

According to Alex. Schmidt, crystallin contains two albuminous substances, one of which is precipitated by carbonic acid, whilst that remaining in solution is coagulated by heat. Simon (*Handb. der angew. medic. Chemie.* 1840, 1, 78, and 83) previously distinguished two albuminous substances in the crystalline lens.

The substance precipitated by carbonic acid behaves precisely like paraglobin, and, as is the case with that body, its slightly alkaline solution is precipitated by heat only when neutral salts are present, as in the fluid of the lens. According to Kühne (*Lehrb.* 404), it is distinguished from paraglobin by the fact that it does not produce fibrin with fibrinogen, and is therefore to be regarded as a peculiar substance.

According to Valenciennes and Frémy, the crystalline lens of mammals contains (1) metalbumin, which occurs in the outer layers of the lens; (2) albumin, which occurs in the central layers, and behaves like egg albumin, but does not assume a blue colour with fuming hydrochloric acid in the air; (3) a fibrin-like substance, soluble in dilute acetic, but not in other acids. The crystalline lens of cetaceans contains metalbumin; that of fishes contains phaconin insoluble in water in the internal, and albumin in the external part.

a. Metalbumin. — The external layers of the lens, which contain the metalbumin, dissolve for the most part in water, forming a solution which coagulates on boiling only after addition of salts or acids, and sometimes only after first evaporating it to a syrup at low temperatures. Metalbumin dissolves in strong hydrochloric acid ~~without~~ assuming a blue colour on exposure to the air. After deducting nearly 1 p. c. of ash, it contains 52·8 p. c. C , 7·3 H., 16·0 N., and 23·9 O., and has, therefore, the composition of albumin.

b. Phaconin, which forms the solid central portion of the crystalline lens of fishes and molluscs, swells up, without dissolving, in water, and becomes opaque in boiling water. It is insoluble in acids, with the exception of acetic acid, in which it dissolves slowly, and it dissolves with difficulty in alkalis. Insoluble in alcohol and ether. Contains 52·11 p. c. C., 7·69 H., 16·53 N., and 23·67 O. (Valenciennes & Frémy).

Globulin of Blood-corpuscles.

The colourless and most abundant constituent of blood-corpuscules was distinguished from albumin by Berzelius as globulin; the red colouring matter of blood was regarded by him as a compound of globulin and hæmatin; moreover, he found in the crystalline lens a body agreeing with globulin. Alex. Schmidt, having found the fibrinoplastic substance in the blood-corpuscles and in the crystalline lens, and supposing it to be formed, together with hæmatin, by the splitting up of hæmoglobin, extended the term globulin to the fibrinoplastic substance, the paraglobin of this work.

According to Kühne, this supposition of Schmidt is erroneous: hæmoglobin yields by decomposition, not fibrinoplasmin, but another albuminous substance, the properties of which will be described under hæmoglobin. It appears, therefore, to be inadmissible to apply the term otherwise than as it was employed in the older statements.

1. When blood-corpuscles, isolated by means of solution of sulphate of soda, are treated with alcohol containing sulphuric acid, there remains a colourless residue, which forms the globulin-sulphuric acid of Berzelius. — It dissolves in pure, but not in saline water containing albumin in solution, and coagulates to a granular mass when the solution is heated, though only at a temperature a few degrees higher than is necessary to coagulate albumin. It combines with acids and bases. Globulin-sulphuric acid, after boiling, is greyish-white, hard, and friable. It swells up in water, becomes translucent, and dissolves only slightly

even on addition of hydrochloric acid. Hydrochlorate of globulin dissolves in water, with the exception of a slight residue, forming a solution which leaves, when evaporated, a translucent residue containing 4·9 p. c. of hydrochloric acid, and soluble in water (Berzelius, *Lehrb.* 3 Aufl. 9, 69).

2. Mulder (*J. pr. Chem.* 17, 329) found in globulin-sulphuric acid prepared by Berzelius's method, and dried at 130°, 53·38 p. c. C., 15·70 N., 7·17 H., and 2·50 SO^3, but appears to regard the body as a mixture of fibrin and albumin.

3. On boiling globulin with moderately dilute sulphuric acid, tyrosine and leucine are formed (Leyer & Köller, *Ann. Pharm.* 83, 332). This globulin was prepared by Leyer & Köller, by separating the clot of coagulated blood from the serum, washing it repeatedly, pressing it in cloths under water, coagulating the filtered liquid by boiling with acetic acid, and boiling the coagulum with alcohol containing sulphuric acid, which left the globulin.

4. According to Lecanu, the globulin of blood-corpuscles is distinguished from serum albumin and egg albumin by its solubility in boiling 20 p. c. alcohol, and by its property of forming with cold water, a solution which is not precipitated by basic acetate of lead. Besides this body, blood-corpuscles contain albumin and a fibrin-like substance, which forms pearly bubbles, and distinctly resists the action of alkalis (Lecanu, *Compt. rend.* 35, 11; Lieb. *Kopp's Jahresber.* 1852, 700).

5. According to Commaille, globulin is contained in a semi-solid condition in blood corpuscles, and forms a platinum-compound which, when obtained from human blood, contains 10·20 to 11·02 p. c., and from ox-blood 10·45 to 10·63 p. c. of platinum (*Chem. Centr.* 1867, 589).

6. The statements of Denis (*Compt. rend.* 47, 996; *Kopp's Jahresber.* 1858, 562; *Mémoire sur le sang*, Paris, 1859) may also be quoted in this place.

The globulin of Denis is an albuminous substance occurring in the corpuscles of the blood and in other parts of the animal organism; it is insoluble in water, and become viscous in non-saturated solutions of chloride of sodium. It is obtained from birds' blood, by mixing the defibrinated blood with from half its volume to an equal volume of a 10 p. c. solution of chloride of sodium, and carefully washing with water the viscous mass which separates on standing for some time. Or from human blood by pressing the clot of venous blood, and heating the thick expressed liquid to 40° or 50° for two hours, with half its volume of a 10 p. c. solution of chloride of sodium. When the very thick liquid thus formed is cautiously diffused through a large quantity of water, without agitating too briskly, the decolorised globulin is left behind.

As thus prepared, globulin forms a soft, white, semi-translucent mass, consisting of microscopic, amorphous, granular lumps. That obtained from birds' blood may be dried below 40° without alteration; that from human blood is rendered insoluble in a 10 p. c. solution of chloride of sodium by drying. Whilst all globulin becomes insoluble in solution of chloride of sodium when kept exposed to the air in the moist state, the fresh substance swells up in a 10 p. c. solution of the salt, and is converted into a thick ropy mass, which is precipitated by water. Heat or contact with alcohol coagulates it, in which state it is not acted on by chloride of sodium, but the coagulum dissolves in boiling weak spirit, re-appearing as the solution cools. The globulin of birds' blood coagulated by alcohol gives up a little fibrin to solution of chloride of sodium (Denis).

Amyloïd.

C. Schmidt. *Ann. Pharm.* 110, 250; *Kopp's Jahresber.* 1859, 615.
A. Kekulé. *Verhandlungen des naturhist.-medic. Vereins zu Heidelberg*, 5, 144; *Schmidt's Jahrb. der ges. Medic.* 103, 7; *Kopp's Jahresber.* 1859, 616. Kekulé & Friedreich. *Virch. Arch.* 16, 50.
Kühne & Rudneff. *Virch. Arch.* 33, 66; *Analyt. Zeitschr.* 4, 132.

Amyloïdal substance.—Discovered by Virchow (*Compt. rend.* 37, 492 and 860) and recognised as a proteide by C. Schmidt. See also *Handbuch*, viii, 75.

Sources. In pathologically degenerated liver and spleen; also in diseased kidneys, brain granulations, and concretions of the prostate gland. Such tissues assume a reddish-brown or more rarely a dirty brown-violet colour, when treated with biniodide of potassium or tincture of iodine. When treated with oil of vitriol and iodine in succession, they acquire a green colour, changing to a dirty violet, or sometimes to blue.

Preparation. The waxy degenerated organ is cut into fine shavings, which are exhausted successively with cold water and weak spirit, to remove any bile-constituents that may be present, and would prevent the action of artificial gastric juice, this process being completed, in case the shavings are still of a dark colour, by boiling them in alcohol containing hydrochloric acid. The shavings are then freed from all solid albuminous matters, by subjecting them to the action of artificial gastric juice at 40°, so long as they continue to yield peptones. The residual substance, if still coloured, is again boiled with acidulated alcohol and with ether; and lastly, the elastic tissue, derived from blood-vessels, is removed by treating the powdered substance with water, alcohol, and ether (Kühne & Rudneff).

Artificial gastric juice is obtained from the stomach of freshly-killed animals by emptying the stomach, washing it with cold water, scraping off the mucous layer, consisting of rennet-cells, with a blunt instrument, and triturating with sand and water. The filtered liquid, mixed with 0·1 p. c. hydrochloric acid, acts as a powerful digestive (Kühne, *Physiol. Chemie*, 33).

Amyloïd forms amorphous, glassy flakes (Kekulé); a white mass (Kühne). Amyloïd, not purified by artificial gastic juice, contains 53·58 p. c. C., 15·04 N., 7·0 H. (Kekulé).

Amyloïd burns when *heated* on platinum foil, emitting an odour of horn, like albumin.—It is insoluble in cold and in boiling *water* (Kekulé). Dissolves on prolonged boiling with water, like coagulated albumin.—Insoluble in cold or boiling dilute acids, and does not swell up therein. Dissolves in fuming *nitric acid*, forming a solution which is rendered turbid by water. Soluble in fuming *hydrochloric acid*, the solution turning violet in the air; on addition of water, the solution throws down hydrochlorate of syntonin, whilst a body precipitable by neutralisation remains in solution (Kühne & Rudneff). Dissolves easily in *oil of vitriol*; on dropping the solution into water and boiling, no sugar is formed (C. Schmidt), but the solution assumes a violet colour with cuprate of potash, without reducing it (Kekulé). Behaves towards *iodine* and *oil of vitriol* in the same way as the tissues containing it, but the colours produced are purer (Kühne & Rudneff).

Amyloïd dissolves in moderately dilute *ammonia*. The solution becomes neutral when evaporated, and does not coagulate even when boiled; when further evaporated it yields tough gelatinous pellicles and flocks, which are coloured by iodine dark reddish-yellow, or, after addition of oil of vitriol, greenish-blue. Sulphuric acid throws down from the ammoniacal solution loose flocks of but slightly altered amyloïd, containing, after drying at 120°, 15·53 p. c. of nitrogen, and 1·3 p. c. of sulphur (Kühne & Rudneff).

The ammoniacal solution is precipitable by *dilute acids*, excess of which does not dissolve the precipitate; by *alum*, *basic acetate of lead*, *sesquichloride of iron*, *corrosive sublimate*, and *tannic acid*; also by *cupric sulphate*, the precipitate being partially soluble in dilute acids, but insoluble in ammonia (Kühne & Rudneff).

Amyloïd swells up in dilute aqueous *alkalis*, and dissolves to a slight extent to a turbid viscid liquid; it dissolves completely in strong alkalis (Kühne & Rudneff); and gradually in boiling dilute potash-ley, with formation of albuminate of potash (Kekulé). In this case a second body insoluble in acetic acid is produced (Kühne & Rudneff).

Amyloïd is insoluble in *baryta-* or *lime-water*, and scarcely swells in these liquids. When boiled with *alkaline solution* of lead oxide, it yields no sulphide of lead. It does not *putrefy*, and is not acted upon by acidulated *pepsin*. It is insoluble in *alcohol* and in *ether* (Kuhne & Rudneff).

Protic Acid.

LIMPRICHT. *Ann. Pharm.* 127, 185; *Kopp's Jahresber.* 1863, 648.

Obtained from the flesh of the roach (*Leuciscus rutilus*). The flesh is exhausted with cold water; the extract is freed from albumin by boiling, and the filtrate is precipitated with baryta-water and concentrated over the water-bath. After standing for 24 hours, the crystals of creatine which have been deposited are removed, and the mother-liquor is precipitated with an acid, whereupon it solidifies, from separation of white flocks of protic acid.

White amorphous bulky precipitate, which on drying at 100° or in a vacuum, becomes amber-yellow, translucent, and brittle. When heated on platinum foil it puffs up and burns without leaving ash. It contains 53·5 to 54·8 p. c. C., 15·8 to 16·1 N., and 7·1 to 7·2 H.

Protic acid is nearly insoluble in cold, and but slightly and slowly soluble in boiling *water*. The solution turns gelatinous when evaporated, and leaves a gelatin-like mass. — Dissolves easily in warm dilute *acetic, hydrochloric*, and *sulphuric acids:* when boiled with dilute sulphuric acid, it yields leucine but no tyrosine. Dissolves very easily in aqueous *ammonia*, in *alkalis*, and *alkaline earths*. These solutions leave on evaporation, amorphous residues soluble in water, the baryta-solution leaving a salt containing 50·6 p. c. C., 6·9 H., and 6·5 Ba. They give precipitates with *metallic salts*. The solution of protic acid in acetic acid is not precipitated by *ferrocyanide of potassium*.

Peptones.

In natural or artificial digestion, which pre-supposes the presence of pepsin and free acid, albuminous substances are converted, first into syntonin and ultimately into peptones. According to Eichwald, these peptones also occur in small quantity in the blood and in larger quantity in old colloïd sacs. They are formed when liquid egg-albumin is kept in contact with mucus for some weeks at the temperature of the body, and out of contact of air (Eichwald). According to Mulder, legumin is converted into peptone by the action of hydrochloric acid alone, but this statement is not confirmed by Brucke's experiments. According to Meissner, legumin boiled with water for a day, yields peptone, but this is denied by W. Schmid. See p 257.

In dilute hydrochloric acid alone, fibrin merely swells up, dissolving only after several days at the temperature of 20°, whereas in hydrochloric acid containing 0·4 p. c. in presence of pepsin, it is rapidly resolved into flocks which dissolve to a turbid liquid. This solution deposits syntonin (Meissner's parapeptone) when neutralised. It is not rendered turbid by boiling when it has been prepared with boiled fibrin, but when made with unboiled fibrin, it contains a body which is coagulated by boiling, probably an albuminous substance enclosed in the fibrin. When digestion has proceeded further, the solution is no longer precipitated by neutralisation, the syntonin being then converted into peptone (Brüche).

Meissner distinguishes as *parapeptone* the precipitable substance formed during digestion, and denies that it possesses the property of passing into peptone. According to him, albuminous substances are resolved into parapeptone, which does not undergo further change, and peptones, which are distinguished as *a*-, *b*-, *c*-peptone and metapeptone.

Preparation. Coagulated white of egg is treated at 40° with artificial digestive fluid (p. 334), containing 0·15 p. c. of hydrochloric acid, until it is completely dissolved, and the solution is not affected by neutralisation with ammonia or by ferrocyanide of potassium or strong mineral acids, which result is attained by repeated warming and fresh additions of acid, in the course of two days, provided the quantity of white of egg taken is not too great. The solution is then filtered and mixed with neutral acetate of lead, and ammonia is dropped into it until the peptone is deposited in flocks, and the supernatant neutral or feebly acid liquid is no longer precipitated by neutral acetate of lead. The precipitate is washed, suspended in slightly ammoniacal water, and decomposed by hydrosulphuric acid; and the filtrate from the sulphide of lead is concentrated and then precipitated by absolute alcohol (Eichwald).

Peptones occurring in animal fluids free from alkaline albuminates may be isolated by dialysis, or by drying and exhaustion with hot water, or by precipitation with alcohol and exhausting the coagulum with water (Eichwald).

According to Eichwald, the peptones obtained from different albuminous substances are probably identical: he distinguishes, however, the peptone obtained from mucin from albumin-peptone. Mulder distinguishes the peptone of gelatigenous tissues from other peptones; it is not precipitable by mercuric chloride, and is not coloured by Millon's mercury-solution, or by boiling with nitric acid and supersaturation with ammonia. Corvisart finds that all peptones exert a dextrorotary action on polarised light, but in various degrees. The relative rotatory powers of fibrin-, syntonin-, gelatin-, and albumin-peptone are as 80 : 100 : 104 : 140.

Properties. Albumin-peptone forms white delicate flocks, or after drying, a yellow, brittle, very hygroscopic mass, containing a very small quantity of ash (Eichwald). According to Lehmann, it contains 1·6 p. c. of sulphur, but Eichwald did not obtain any sulphide by boiling it with strong potash-ley. — The aqueous solution diffuses very easily through parchment-paper.

Dissolves very easily in *water*, forming a solution which is not affected by boiling, or by *acids*, *alkalis*, or concentrated solutions of *salts*, or by *ferrocyanide of potassium* and acetic acid. The solution acquires a yellow colour when mixed with strong *nitric acid* or with *ammonia*, and produces with Millon's *mercury-solution*, brown flocks which turn red on warming.

Neutral (not acid) solutions of peptone are precipitated, immediately when strong, and after standing some time when more dilute: white by *neutral acetate of lead*, yellowish-brown by *ferric chloride*, white by *mercuric chloride*, yellow by *bichloride of platinum*, and white, gradually turning dark brown, by *silver salts*. Neutral or faintly acid, but not alkaline solutions give brown flocculent precipitates with *tannic acid*. *Alcohol* precipitates peptone from neutral, but not from acid or alkaline solutions (Eichwald, *Wurzb. Medic. Zeitschr.* 5, 322).

¶ According to E. Brücke (*Wien. Akad. Ber.* 61, 250; *Chem. Soc. J.* [2] 9, 410), albumin-peptone is also precipitated by metatungstic acid, phosphomolybdic acid, and potassio-mercuric iodide. He particularises two peptones—1. One soluble in alcohol and water, which he names *alkophyr;* 2. Another easily soluble in water but insoluble in alcohol, which he calls *hydrophyr*. They are both very similar to albumin, and have the same reactions, with the exception of the precipitation by potassium ferrocyanide, and the red coloration with sulphuric acid and sugar; on the other hand, they give a purple colour with cupric oxide and potash. 3. There is sometimes a third substance associated with the peptones, which gives the above-mentioned red coloration. This substance was obtained by artificial digestion of blood-fibrin, neutralisation, evaporation, and extraction with alcohol, which dissolves this compound and leaves the hydrophyr undissolved. Neither Mulder nor Lehmann found anything insoluble in alcohol. Brücke believes that in their experiments the digestion was carried much further, as he finds that there is always a portion insoluble in 96 p.c. alcohol, which at the commencement of the digestion is *hydrophyr*, but later, another compound which does not yield a purple colour with copper oxide and potash. In some albumin which had been submitted to artificial digestion for three months, there was no residue of *hydrophyr* insoluble in alcohol, but the solution contained *alkophyr*. Precipitated *hydrophyr* can be partially dissolved by treating it with acetic acid and alcohol. Neither *alkophyr* nor *hydrophyr* was contained in albumin or in the gastric juice employed. The reaction with copper oxide and potash is a very delicate test for albuminous substances and peptone. A very small quantity of the cupric ammonia or potash solution, together with a little cupric sulphate, is added to the albuminous or peptone substance, whereupon the excess of copper oxide above that required for the production of the purple-red compound falls to the bottom. The purple coloration is occasioned by the absorption of the green portion of the spectrum.

When casein (obtained by precipitating milk with acetic or hydrochloric acid, and freed as much as possible from fat by means of ether) is digested, for periods varying from 5 hours to 11 days, at 40°—45°, with artificial gastric juice (prepared by treating the mucous membrane of a pig's stomach with water containing 3 p. c. hydrochloric acid) a large portion dissolves, but a certain portion always remains undissolved however long the digestion may be continued. When serum-albumin and casein were digested for equal times, the quantity of albumin dissolved was one-third less than that of the casein.

The digested solution contains pepsin, peptones, leucine and tyrosine. The alcoholic extract of the products of digestion treated with baryta-water, yields a brown, transparent, deliquescent mass, which appears to be a compound of peptone with baryta. When purified with alcohol and ether, it forms a white non-deliquescent powder containing chlorine. The proportion between the chlorine and the barium in this body is by no means constant. Its specific rotatory power is 63·2°; and if the chlorine and barium be regarded as inactive, the rotation calculated for the organic substance alone is 84°. By precipitating the barium-compound with sulphate of zinc or copper, compounds of peptone with zinc oxide and cupric oxide are obtained.

The undigested residue of the casein — the *dyspeptone* of Meissner—consists of two substances, one of which, A, is soluble, the other, B, insoluble in carbonate of soda. When A is precipitated from this solution by hydrochloric acid, it dissolves in great part if digested anew with gastric juice; but a certain amount always remains undissolved. This substance, when purified by alcohol and ether, forms a yellowish-white dusty powder containing 48·5 p. c. C., 13·3 N., 7·1 H., 4·6 P., and 26·5 O., corresponding nearly with the formula $C^{54}N^{6}H^{47}PO^{22}$ (calc. 48·9 C., 12·7 N., 7·1 H., 4·7 P., 26·6 O.). When moistened with water, it has an acid reaction, and appears partly to expel carbonic acid from carbonate of soda. On dry distillation it emits an irritating smell, not at all like that of albuminous substances. — The body B resembles albumin in its reactions, and contains sulphur and phosphorus, but its exact composition has not yet been determined. It is possibly an isomeric modification of casein; but A, from its reactions and comparatively simple composition, does not appear to belong to the proteide group, but rather to be a product of the decomposition of casein, which must accordingly be regarded, like vitellin and hæmoglobin, as a compound of an albuminous or proteide substance with a compound of a different class (Lubavin. Hoppe-Seyler, *Med. Chem. Unters.* 1871, 463). ¶

On peptones, see further *Handbuch*, viii, 34; *Lehmann's Physiological Chemistry*, ii, 53, 56. The following memoirs, selected from the voluminous literature of the subject, may also be referred to :—

LEHMANN. *Lehrb. der Physiol. Chemie*, 2 Aufl. 1, 318.

MULDER. *Donder's Arch. für holländ. Beiträge* 2, 1; *Schmidt's Jahrb. für. ges. Medecin*, 101, 151.

MIALHE & PRESSAT. *Compt. rend.* 33, 450.—MIALHE. *N. J. Pharm.* 10, 161.

CORVISART. *Schmidt's Jahrb.* 102, 244; 108, 287.—*Ann. Pharm.* 125, 126; *Schmidt's Jahrb.* 118, 278.

MEISSNER. *Henle & Pfeuffer's Zeitschr. f. ration. Medic.* 3 Reihe, 7, 1; *Schmidt's Jahrb.* 104, 147.—*Henle & Pf.* 8, 280; *Schmidt's Jahrb.* 105, 148.—MEISSNER & THIRY. *Henle & Pf.* 10, 1; *Schmidt's Jahrb.* 108, 283.—MEISSNER & BÜTTNER. *Henle & Pf.* 12, 46; *Schmidt's Jahrb.* 114, 157.—MEISSNER & J. DE BARRY. *Henle & Pf.* 14, 303.—MEISSNER & KIRCHNER. *Henle & Pf.* 14, 311.—MEISSNER & THIRY. *Henle & Pf.* 14, 78; also *Schmidt's Jahrb.* 118, 279 and 281.

BRINTON. *Schmidt's Jahrb.* 104, 151.

BRUCKE. *Wien. Acad. Ber.* 37; 131; *Schmidt's Jahrb.* 105, 144.

MARCET. *Ann. Pharm.* 120, 250; *Schmidt's Jahrb.* 114, 162.

V. WITTICH. *Schmidt's Jahrb.* 118, 283.—V. WITTICH & COHN. *Schmidt's Jahrb.* 118, 278.

J. DE BARRY. *Tübing Medic. Unters.* 1, 76.

DIAKONOW. *Tübing Medic. Unters.* 1, 241.

Pepsin.

BRÜCKE. *Wien. Acad. Ber.* 43, 2, Abth. 601; *Chem. Centr.* 1861, 929 and 956; *Jahresber.* 1861, 789.

Verdauungsstoff. The constituent of the gastric juice which effects the conversion of albuminous substances into peptones. Named by Schwann. See the older investigations, *Handbuch* viii, 26; *Lehmann's Physiological Chemistry*, 2, 46; further: Vogel (*N. J. Pharm.* 2, 273; *Berzel. Jahresber.* 23, 605); J. Vogel (*Ann. Pharm.* 30, 37); C. G. Mitscherlich (*Pogg.* 40, 128).

The pepsin of commerce is either the mucus of the stomach scraped off and dried, or a mixture of pepsin, peptones, and starch, containing lactic acid. See Guibourt (*J. Pharm. Chim.* [4] 2, 81).

The glandular layer of a pig's stomach is digested with aqueous phosphoric acid till it becomes disintegrated; the solution is mixed with so much lime-water that it turns litmus blue; and the precipitate, which carries down nearly the whole of the pepsin with it, is dissolved in dilute hydrochloric acid. This solution is again precipitated with lime water; the precipitate is dissolved in dilute hydrochloric acid; and the solution is submitted to prolonged agitation with a cold saturated solution of cholesterin in a mixture of 4 parts of 94 p. c. alcohol and 1 part of ether. A white emulsion is thus formed, containing finely divided cholesterin, which takes up the pepsin. This emulsion is collected, washed with water containing acetic acid and with pure water, and lastly agitated with ether free from alcohol so long as it gives up cholesterin. The pepsin then remains in aqueous solution, which is to be freed from ether by exposure to the air and from a little mucus by filtration.

Gastric juice obtained from a fistula in the stomach of a dog by mechanical or electrical irritation of the empty stomach, may, provided it contains no albumin or acidalbumin, be freed from acid, salts, and peptones by dialysis, the pepsin then remaining behind on the dialyser (Krasilnikow, *Tübing. medic. Untersuch.* 1, 240).

Aqueous pepsin is colourless and neutral, and is not affected by strong nitric acid, tincture of iodine, corrosive sublimate, nitrate of silver, or tannic acid. It produces a turbidity in neutral acetate of lead, even when acidified with acetic acid; also in basic acetate of lead and bichloride of platinum. One drop added to 5 c.c. of aqueous acid containing 0·1 p. c. of hydrochloric acid, dissolves a flock of fibrin in the course of an hour. Finely divided phosphate of lime, animal charcoal, and sulphur, withdraw pepsin from its aqueous solution (Brücke).

Mucin.

FIGUIER. *J. Pharm.* 26, 113.
GOBLEY. *N. J. Pharm.* 33, 161.
ROLLET. *Wien. Acad. Ber.* 39, 308; *Chem. Centr.* 1860, 401; *Jahresber.* 1860, 567.
E. EICHWALD, jun. *Würzb. medic. Zeitschr.* 5, 281; *Ann. Pharm.* 134, 177; *Chem. Centr.* 1866, 209; *Jahresber.* 1865, 649.

To be distinguished from the mucin of wheat-gluten.

Source and Formation. 1. In the vineyard snail (*Helix pomatia*), the mucus of which was previously examined by Figuier and Gobley (Eichwald.) On the mucus of *Limax agrestis* and limacin, see below.

2. In many mucous fluids of the animal organism, especially in the fluid contents of colloïd sacs, in the mucous secretion of the respiratory passages, in lymph glands, salivary glands, sarcomas, and fibroïds (Eichwald). Hence the products investigated by Scherer, Kemp, Gorup-Besanez, Städeler, and Cramer belong to this place, notwithstanding their divergent composition. See below.

3. The intercellular substance of connective tissue yields mucin by treatment with lime-water (Rollet; Eichwald).

Preparation. A. *From Vineyard Snails.* The snails freed from shells and cut up, are triturated with sand to a pulp, which is boiled with water. The liquid is filtered hot, and the dirty brown filtrate, which contains mucin and albumin-peptones, but no albumin, is precipitated with excess of acetic acid. The precipitate is washed by decantation, first with water containing acetic acid, and afterwards, when the washings are no longer rendered turbid by tannic acid, with pure water, to free it from acid. It is then dissolved in dilute lime-water, and again precipitated with a large excess of acetic acid. The flocks thereby thrown down are again washed with dilute acetic acid, so long as the washings contain lime, hydrochloric acid, or peptone precipitable by tannic acid, and then with pure water till the mucin begins to swell up and run turbid through the filter. Strong spirit is then poured upon them, and they are preserved in that liquid (Eichwald).

B. Eichwald obtained mucin from mucous *fluids of the animal organism* in the same way as from snails. Such liquids, however, when thin, require to be warmed to 40° after precipitation with acetic acid, whilst thicker or viscid masses must be suspended in water before precipitation. The mucin thrown down often contains much albumin, and in that case is to be washed with water containing acetic acid till the washings cease to precipitate ferrocyanide of potassium or tannic acid. Sometimes it contains also plastic elements, which cannot always be separated by filtration, but only by deposition and decantation.

C. *From the connective tissue of the higher animals.* Sinews cut into fine shavings are freed from albumin and albuminates of the alkalis by washing with warm water and pressing in linen cloths till the washings are no longer precipitated by acetic acid and ferrocyanide of potassium. The residue is then digested with lime-water, in which the sinews swell up and become disintegrated; and after standing for 12 hours the product is exhausted two or three times more with lime-water. The filtered extracts are precipitated with a large excess of strong acetic acid, and the flocks of mucin thereby thrown down are purified by again dissolving them in lime-water and precipitating as before, and finally by washing them in closed vessels (Eichwald; Rollet). If the acetic acid employed be dilute or in too small quantity, the liquid is difficult to filter, and albumin is thrown down with the mucin (Eichwald).

Mucin is pure if, when it is mixed with water and acetic acid, and filtered, the filtrate gives no precipitate with ferrocyanide of potassium or tannic acid.

Properties. The mucin of snails, precipitated with alcohol, forms dense brown-grey flocks; that obtained from tissues or animal fluids is white or greyish-white. — After drying it forms a brown gelatin-like mass, difficult to pulverise (Eichwald).

	Kemp.	Mulder.	Scherer. *a.*	Scherer. *b.*	Gorup-Besanez.	Cramer. *at* 125°—130°.	Eichwald. 110°.
C	52·00	50·78	52·18	50·62	51-68	51·04	48·94
N	14·54	9·42	12·64	10·01	13·22	17·69	8·50
H	7·80	6·65	7·01	6·58	7·06	7·24	6·81
O	25·66	33·15	28·17	32·79	28·04	24·03	35 75
	100·00	100·00	100·00	100·00	100·00	100·00	100·00

Scherer's mucin was obtained from a large cyst between the trachea and œsophagus of a man. — The viscid ropy contents of the cyst exhibited the characters described in Lehmann's Physiol. Chemistry, ii, 371, 372. *a.* When diluted with warm water, filtered, and precipitated with alcohol, it throws down a coagulum, which was purified by boiling it with alcohol, dissolving in water, precipitating with alcohol, drying, triturating, and exhausting with alcohol and ether. The product is white, friable, free from sulphur, soluble in water, and contains 4·1 p. c. of ash, consisting of phosphate of lime with alkaline carbonates.—*b.* When the aqueous solution of this alkaline mucin is precipitated with acetic acid, a purer mucin is thrown down, which is still to be washed with water, boiling alcohol, and ether (Scherer, *Ann. Pharm.* 57, 196).

Kemp and Gorup-Besanez examined bile-mucus; Cramer, the mucus of the salivary glands, further particulars of which substances are given below. Mulder's analysis (*Scheik. Onderzoek.* 1, 34; *Ann. Pharm* 48, 366) refers to the so-called *Sternschuppenmaterie*, which appears to be the mucus of the oviduct of the frog, and is regarded by Eichwald as mucin.

According to Eichwald, the percentage of nitrogen in mucin was formerly stated too high, in consequence of its containing albumin-peptone.

Decompositions. 1. Mucin acquires a straw-yellow colour when boiled with dilute *nitric acid*, and dissolves in the boiling strong acid, forming a solution from which ammonia throws down flocks, soluble with brown colour in excess.—2. Warm strong *hydrochloric acid* dissolves mucin with dirty-brown colour (Eichwald). Rollet's mucin dissolves gradually in hydrochloric acid, with blue colour.

Mucin is resolved by boiling for a short time with *mineral acids*, or by more prolonged boiling with moderately strong *acetic acid*, into acid albumin and grape-sugar, other products being probably formed at the same time (Eichwald). On the acidalbumin, see p. 313. The grape-sugar remains in solution after filtering off the acidalbumin, and is obtained by neutralising the sulphuric acid solution with milk of lime, evaporating the filtrate, and exhausting the residue with alcohol. The extract left on evaporating the alcoholic solution behaves like grape-sugar towards alkaline solution of copper and potash-ley (Eichwald).

3. Mucin assumes a rose-red colour when warmed with *mercurous and mercuric nitrate* (Eichwald), and a red to dark-violet colour with *oil of vitriol* and *sugar* (Rollet).—4. When boiled with *lime-water* it yields mucus-peptone (p. 344) (Eichwald).

Dry mucin is insoluble in *water*, either cold or hot. Moist mucin, preserved under alcohol, readily swells up in water, without dissolving. Water shaken with mucin remains turbid for some time, more so in the lower layers than in the upper; the latter deposit a part of the mucin when diluted with water, and another portion, which cannot be separated by filtration, only after long standing. Addition of a little *acid* throws down dense flocks, which dissolve in strong, but not in dilute mineral acids. Mucin is insoluble in aqueous *acetic* and *oxalic acids*, and in *hydrochloric acid* of $\frac{1}{10}$th p. c. Moderately dilute mineral acids dissolve it partially; strong hydrochloric, sulphuric, and nitric acids completely, forming clear solutions precipitable by water and alkalis.—Strong aqueous chloride of sodium and other alkali-salts take up mucin, forming opalescent frothing liquids, which are partially precipitable by water (Eichwald).

Mucin dissolves easily in aqueous *alkalis*, *alkaline earths*, and *ammonia*, forming therewith clear solutions, susceptible of filtration, even when the solvents are very dilute. A solution made with excess of mucin is neutral to litmus (Rollet; Eichwald). Alkaline solutions are precipitated by mineral and organic acids, with the exception of carbonic acid; the precipitate produced by acetic acid is free from the acid. The precipitates thus produced are easily soluble in excess of the acids; in hydrochloric acid more especially in presence of chloride of sodium (Eichwald).

Neutral or slightly alkaline solutions of mucin in aqueous alkalis are not affected by boiling; they are not precipitated by *ferric chloride*, *cupric sulphate*, *mercuric chloride*, or *silver nitrate*, provided the alkali is not in excess. They are rendered opalescent by *neutral acetate of lead*, and precipitated completely in flocks by the *basic acetate*, but are not affected by *tannic acid.*—Acid solutions of mucin are precipitated by *ferrocyanide of potassium* only on neutralisation (Eichwald).

Mucin dissolved in alkalis does not diffuse through parchment-paper. It is coagulated by alcohol, and after pressing, redissolves in water, forming alkaline or neutral solutions, according to the reaction of the original liquid (Eichwald).

Alcohol causes mucin suspended in water to collect in dense flocks, which, when freed from alcohol by washing, again diffuse in water (Eichwald).

Appendix to Mucin.

1. Eichwald's *Acidalbumin.*—Obtained, together with grape-sugar, by boiling mucin [or paraglobin (Eichwald, *Chem. Centr.* 1869, 566)] with dilute acids.

a. Mucin suspended in water is mixed with dilute sulphuric acid, and the turbid frothing liquid is heated to boiling, whereupon the mucin swells up and dissolves, the liquid afterwards assuming a brown colour, and depositing dark flocks. The decomposition is complete when the supernatant liquid, after being allowed to cool and neutralised with alkali, no longer gives a precipitate with acetic acid: a precipitate insoluble in excess of acetic acid indicates undecomposed mucin; a precipitate soluble in excess consists of acidalbumin, remaining in solution in consequence of too little sulphuric acid being employed.—After cooling, the flocks are collected and washed, till they begin to dissolve in water.

b. Mucin is boiled with moderately dilute acetic acid for an hour or two, or until it dissolves to a clear brown liquid; the filtrate is neutralised with ammonia-water, and the flocks thereby thrown down are washed by decantation, first with aqueous acetate of ammonia, then with alcohol, and dried. Before analysis it is to be washed with alcohol and ether, and then contains 53·62 p. c. C., 13·18 N., 7·15 H., and 26·05 O., and is free from sulphur and ash.

Acidalbumin obtained according to *a*, forms brown flocks, which dry up to a brown friable mass, insoluble in cold or boiling water, and in very weak potash-ley. Moist acidalbumin dissolves easily in *water*, forming a brownish frothing liquid, which is susceptible of filtration, and is not affected by boiling, and not precipitated by dilute mineral acids, by dilute or strong acetic acid, or by concentrated solution of chloride of sodium, but gives a precipitate when mixed first with chloride of sodium, then with a small quantity of acid. Strong mineral acids in excess produce insoluble flocks with this aqueous acid albumin; ferric chloride, neutral and basic acetates of lead, cupric sulphate, mercuric chloride, silver nitrate, and tannic acid precipitate it completely; ferrocyanide of potassium precipitates it only after addition of an acid. — Moist acidalbumin is insoluble in strong, but easily soluble in very dilute *mineral acids* (and in *vegetable acids* of all strengths), and is deposited from these solutions on evaporation, in flocks which re-dissolve when the solution is again diluted. The solutions are precipitated by ferrocyanide of potassium, tannic acid, excess of basic acetate of lead, and incompletely by metallic salts. — Acidalbumin is insoluble in strong aqueous *solutions of salts*, such as acetate of ammonia, acetate of soda, chloride of sodium, sulphate of potash. — It dissolves very easily in aqueous *alkalis*, from which it is precipitated by metallic salts and tannic acid; acids precipitate the alkaline solutions only in presence of a large quantity of alkali or alkaline salt.

Acidalbumin is precipitated from its aqueous solution by weak spirit and absolute *alcohol;* prolonged contact with the latter renders it insoluble in water.

2. Eichwald's *Mucus peptone.* — Obtained by decomposing mucin with boiling lime-water. Occurs ready formed in fluids containing mucus, which have remained stagnant for some time in living bodies.

Mucin is dissolved in excess of lime-water, and the solution is mixed with three times its volume of water and boiled for two or three hours, or until a test-portion no longer gives a precipitate with acetic acid. The lime is then separated by means of carbonic acid, and the filtrate is concentrated and precipitated with alcohol, which throws down the peptone in greyish-white delicate flocks, drying up to a yellow mass.

Mucus peptone dissolves easily in cold water, even after drying, forming a solution which diffuses readily through parchment-paper, and is not precipitated by aqueous acids, salts, or alkalis in the cold, but is decomposed by boiling with dilute acids, with separation of white flocks. Aqueous mucus peptone is coloured brownish by tincture of iodine; it does not colour or reduce alkaline solution of cupric oxide, even after contact with saliva, or on boiling with acids. It gives with basic acetate of lead, dirty-white flocks, soluble in acetic acid; and with a mixture of mercurous and mercuric nitrate, flocks which turn red when warmed. It is not precipitable by neutral acetate of lead, ferric chloride, cupric sulphate, mercuric chloride, nitrate of silver, bichloride of platinum, or tannic acid, even after addition of acids.

3. *Animal mucus only partially agreeing with Mucin.* See the analyses p. 341. — Occurs of various degrees of consistence and viscidity, owing probably to differences in the amounts of alkali which it contains (Städeler).

Mucus of Limax agrestis. — Forms a colourless translucent slimy fluid of alkaline reaction, solidifying to a jelly on evaporation, susceptible of filtration when diluted, and precipitable by acids, metallic salts, and tannic acid. After drying at the ordinary temperature, it redissolves in water to a ropy liquid, but when dried at 100° it becomes insoluble. The mucus dissolves in ammoniacal or slightly alkaline water, or in lime-water, forming solutions from which acids throw down a translucent jelly. These alkaline solutions, as well as the original mucus, become limpid on standing for some days and are then not precipitable by acids, a substance coagulable by heat like albumin being formed (Braconnot, *N. Ann. Chim. Phys.* 16, 313). The property was also observed by Gobley in the mucus of the vineyard snail.

Braconnot's *limacin*, likewise from *Limax agrestis*, is obtained by boiling the snails with water, evaporating, exhausting the residue with small quantities of cold water to remove extractive matters, boiling with water, and filtering; the limacin is deposited from the filtrate as it cools. It is white, friable, and slightly soluble in water while in the moist state; the somewhat slimy solution in boiling water deposits it in white flocks on cooling. Its aqueous solution precipitates tannic acid and metallic salts. Limacin dissolves easily in alkaline water, forming a solution which does not blacken silver, and yields with acids a dead-white precipitate soluble in excess of acid. The solution in hydrochloric acid does not assume a blue colour. Limacin dissolves in boiling alcohol (Braconnot, *N. Ann. Chim. Phys.* 16, 319). Gobley also obtained this body (*N. J. Pharm.* 33, 164).

Mucus of the Gall-bladder.—Precipitable by alcohol from ox-gall. After precipitation it is insoluble in water but swells up therein. Becomes translucent and gelatinous in potash-ley and dissolves to a slight extent in weak potash, from which it is precipitated by acids. Leaves 1 p. c. of phosphate of lime when burnt.—The mucus precipitated from bile by acetic acid is green after drying, owing to the presence of biliverdin; when mixed in the moist state with not too much potash, it sometimes becomes elastic, but generally gelatinous and translucent (Berzelius, *Ann. Pharm.* 43, 7, and 59.—Tiedemann & Gmelin, *Die Verdauung*, 1, 43).

The mucus precipitated from ox-gall by alcohol, when washed with alcohol and ether and dried below 100°, is grey and transparent, and contains sulphur and 10 p. c. of ash. It becomes translucent in water, without dissolving. The mucus precipitated by absolute alcohol cannot be suspended, even while moist, but swells up in water at 120° and dissolves at 200° (Kemp, *Ann. Pharm.* 43, 115).

A solution of the mucus of human bile in aqueous potash gives no precipitate with hydrochloric acid, except after addition of tincture of galls (Fromherz & Gugert).—The mucus from the gall-bladder of an apoplectic patient gave precipitates with alcohol and dilute acids; it then swelled up in water and partially dissolved. After boiling with alcohol and ether and drying, it was white, brittle, and quite insoluble in water (Gorup-Besanez, *Ann. Pharm.* 59, 153).

The mucus scraped from the small intestines of the dog or horse, after being washed with cold water, digested in dilute hydrochloric acid, and again washed with water, dissolves, with the exception of a few flocks, in very dilute potash or ammonia-water, and is precipitated therefrom by acids. It dissolves for the most part in warm acetic acid (Gmelin).—The mucus which is deposited from urine dissolves easily in alkalis and is not precipitated by acids (Berzelius).

Mucin of the Salivary glands. Ptyalin. Speichelstoff.—The fluid contents of the salivary glands contains mucin (Eichwald). Mucin is contained in chorda-saliva and more abundantly in symphaticus-saliva, but not in parotid-saliva. When symphaticus-saliva is mixed with excess of acetic acid, and then beaten with a glass rod, it separates into a fluid which is no longer ropy, and solid masses of mucin (Kühne, *Physiol. Chemie.* 11).

Berzelius (*Lehrb.* 3 Aufl. 9·217) distinguished in mixed saliva (the mixed fluids of the cavity of the mouth) *mucus*, a constituent of the secretion of the mucous secretion of the mouth itself, and *ptyalin*, derived from the secretion of the salivary glands. When saliva diluted with water is left to itself, a portion of the mucus separates as a coherent mass. On evaporating the filtrate, washing the residue with alcohol, which takes up flesh-extract and salts, neutralising the undissolved slightly alkaline portion with acetic acid, and evaporating, a residue is left from which alcohol takes up acetate, leaving a mixture of ptyalin soluble in cold water, and mucus insoluble therein. Ptyalin is colourless and transparent; when placed in water it turns opaque, white, and slimy, and dissolves to a clear liquid, which is not precipitated by boiling, or by the addition of basic acetate of lead, mercuric chloride, tannic acid, or even of strong acids. — Mucus is opaque and insoluble in water: it coagulates in contact with acids, dissolves in alkalis, and is precipitated by acids. Hence the ptyalin appears to be mucus-peptone, the mucus probably mucin (Kr.).

Similarly Mitscherlich distinguishes mucus and ptyalin in parotid saliva. Ptyalin is obtained as a yellowish-brown hygroscopic mass when the alkali of the saliva is not neutralised. Prepared by the method of Berzelius, it has the properties mentioned above, and after evaporation to dryness without heat, is completely soluble in water, from which it is precipitated by alcohol (Mitscherlich).

Ptyalin dissolved in water gives with cupric sulphate a green precipitate, the filtrate from which is also green. Copper cannot be detected either in the precipitate or the filtrate until the organic matter is destroyed (C. G. Mitscherlich, *Pogg.* 40, 126).

For the statements of Tiedemann & Gmelin, Simon, Wright, Tilanus, and Lehmann on ptyalin, see *Handbuch*, viii, 7; Lehmann's *Physiological Chemistry*, ii, 13—17; see also Hünefield (*Schweig.* 60, 139), and Guibourt (*J. Chim. Méd.* 9, 197).

The *mucus of saliva* becomes transparent and horny in sulphuric, hydrochloric, or acetic acid, without dissolving or giving up to the acid phosphate of lime, which remains, however, on incineration (Berzelius). — The mucus, which is insoluble in water, assumes a red colour with oil of vitriol, and forms a slightly blue solution with cold, or more easily with boiling hydrochloric acid. Ammonia causes it to swell, without dissolving it, even on warming. Potash dissolves it incompletely when heated. Acetic acid behaves like ammonia (C. G. Mitscherlich, *Pogg.* 27, 340).

The *Mucus of the Nose* and *the Respiratory passages* is coagulated by nitric acid. With 19 parts of water it forms a transparent albumin-like mass, dissolves in dilute sulphuric acid, and coagulates in acetic acid without dissolving therein, even on boiling: in potash-ley it first becomes viscid and then dissolves (Berzelius). The washed mucus of the nose takes up copper from dilute solution of cupric sulphate, and partially dissolves in it: the undissolved portion is taken up by hydrochloric and sulphuric acids, but not by acetic acid (Mitscherlich, *Pogg.* 40, 132).

The *Mucous substance of the Salivary glands*, according to the analyses of Cramer given above, has not the composition of mucin. According to Städeler, it occurs also in the mucous membranes and in the white of hens' eggs, and may be obtained from the salivary glands by the following process. The glands are triturated with powdered glass; the albumin and other substances readily soluble in water are removed by agitating two or three times with water; and the residue is further exhausted with water. The ropy extracts thus obtained (which may be filtered after dilution) become viscid on addition of acetic acid, owing to partial abstraction of alkali, and afterwards deposit white flocks of mucin, which is to be purified by washing with water, alcohol, and ether.—As thus obtained, mucin forms an elastic mass resembling blood-fibrin (Städeler), and still containing, according to Cramer's analysis, 1·84 p. c. of ash. After precipitation with acetic acid, it is no longer soluble in cold or warm water, but on prolonged boiling, a portion dissolves, and is again precipitated in white flocks by acetic acid. Glacial acetic acid causes it to swell up to a jelly, and dissolves it on prolonged boiling; alkalis throw down from the solution bulky flocks. Mucin boiled with dilute sulphuric acid yields leucine and 7 p. c. of its weight of tyrosine (Städeler, *Ann. Pharm.* 111, 14; Cramer, *Dissert. über Seide und thierischen Schleim*, Zur'ch, 1863, 32).

On *Mucin* from the *Submaxillary gland*, see ADDENDA to this volume.

Ptyalin.—This term, originally applied to Berzelius's salivary matter, has lately been extended to the sugar-forming ferment of saliva, which according to Cohnheim, may be obtained as follows:—

Fresh human saliva, obtained by filling the mouth with ether-vapour, is strongly acidified with aqueous phosphoric acid, and lime-water is added to alkaline reaction. A precipitate is thus produced, containing, besides tricalcic phosphate, albuminous substances and ptyalin: when washed with water it gives up the ptyalin, which is precipitated by alcohol from the first wash-waters in delicate white flocks, and freed from phosphates by repeatedly precipitating its aqueous solution with absolute alcohol. The product is washed with weak spirit, and then with a little water, and dried at a low temperature.—Nitrogenous; burns on platinum foil, evolving an odour of burnt horn, and leaving no ash. Does not yield xanthoproteic acid with nitric acid. Dissolves easily in water, forming a solution which is precipitated by neutral and basic acetates of lead, but not by mercuric chloride, platinic chloride, or tannic acid.

Ptyalin rapidly produces sugar from dry starch, starch-paste, or dextrin. The conversion takes place most rapidly at 35°: ptyalin is inactive at 60°. The action takes place in neutral, slightly acid, or slightly alkaline solutions, and when stopped by the presence of rather more acid or alkali, is set up again by neutralisation: very large quantities of acid, however, stop the action altogether. The formation of sugar takes place the more slowly the smaller the quantity of ptyalin present, but when 1·5 to 2·5 p. c. of sugar has been formed, even strong solutions of ptyalin cease to act until the proportion of sugar is reduced by dilution. In solutions sufficiently dilute, very little ptyalin produces large quantities of sugar, apparently without undergoing alteration in itself.

Saliva effects the conversion of starch into sugar, owing to the ptyalin it contains, and loses this property when the ptyalin is separated. Raw starch digested with saliva at a temperature not exceeding 35°, loses its property of turning blue with iodine: the granulose of the starch-granules is dissolved as sugar, and a skeleton of starch cellulose remains. Thick starch-paste becomes mobile in contact with saliva. See also *Handbuch.* viii, 19; *Lehmann's Physiol. Chemistry*, ii, 31; iii, 499.

Ptyalin does not affect cane-sugar, amygdalin, or salicin. See, on the contrary, Städeler (xv, 438, 14); Cohnheim (*Kühne's Physiol. Chemie*, 18; *Virch. Arch.* 28, 241).

Keratin or Horn-substance.

Vauquelin. *Ann. Chim.* 58, 41; *N. Gehl.* 2, 222.
J. Scherer. *Ann. Pharm.* 40, 53; *Berzel. Jahresber.* 22, 571.
van Laer. *Scheikund. Onderzoek.* 2, Stuk 75; *Berzel. Jahresber.* 23, 617.
Hinterberger. *Ann. Pharm*, 71, 70; *Jahresber.* 1849, 502.
v. Bibra. *Ann. Pharm.* 96, 289; *Jahresber.* 1855, 750.

The constituent of the epidermis and of epithelium, in which it exists in the membranous form. In the compact state it forms hair, horns, nails, claws, and feathers.—It is obtained pure by boiling these substances with water, alcohol, and ether.

Horn-substance is of various colours, but no colouring matter can be separated from it: hence v. Bibra concludes that the colour is due to structure. It is hard and elastic: when heated it softens and melts.

	v. Laer.	Scherer.					
	Hair, dried at 120°.	*Hair.*	*Nails.*	*Enveloping Membrane of the Egg.*	*Buffalo-horn.*	*Feathers.*	*Quills.*
C	49·70	50·24	50·30	49·98	50·86	51·78	52·06
N	17·14	17·14		16·76	17·28	17·68	17·89
H	6·36	6·69	6·82	6·61	6·71	7·11	7·21
Ash		0·3—2·0	0·5	1·3	0·7	1·8	0·7

		Gorup-Besanez.	Hinterberger.
	Epidermis.	*Epithelium, at* 120°	*Ox-horn,* 100°.
C	50·20	51·63	50·65
N	17·22	16·64	16·23
H	6·78	7·11	6·67
Ash	1·0	1·17	1·9

The hair analysed by v. Laer contained 5 p. c., the epithelium of Gorup-Besanez 2·48 p. c. of sulphur. The proportion of sulphur in horny structures varies greatly, even in one and the same tissue. The hoof of the elk was found to contain 0·87; that of the deer 3·02 p. c. Human hair contained, on the average, 4·5 p. c. of sulphur: in one case, however, the percentage sank to 3·85, while in another case it rose to 8·05, this last proportion being found in red hair, which from other persons contained no abnormal amount of sulphur (v. Bibra). See also *Handbuch*, viii, 467 and 468.—The organic substance of hair and horn is free from phosphorus (v. Bibra).

According to Werner Schmid (*Zeitschr. f. Chem.* [2], 4, 126), the entire human skin contains, at 100°, 44·25 p. c. C. (after deducting ash, 45·5 p. c. C.), 12·29 N., 6·75 H., 1·14 S., 2·81 ash, and 32·76 O., and, therefore, much less carbon and nitrogen than horn-substance.

Horn yields by dry distillation carbonic acid and hydrocarbon gases, water, hydrocyanic acid, carbonate of ammonia, and a stinking oil, leaving charcoal. — Hair yields more sulphur and but little gas (Vauquelin). Feathers give off a sulphuretted gas which evolves much heat with peroxide of lead, and yield a distillate containing pyrrol and other volatile bases (Williams, *Ann. Pharm.* 109, 127).

Articles made of horn soften when warmed, and retain the shape given to them after rapid cooling. Cracked quills, dipped in boiling water for a minute and then in cold water till perfectly cold, show no trace of the cracks (Böttger, *Polyt. Notizbl.* 1858, 16 ; *Kopp's Jahresber.* 1858, 543).

The human epidermis swells up considerably in boiling water (John). Hair is insoluble in water at 100° (Vauquelin). Hair cleaned with cold water and spirit yields, when submitted to prolonged digestion with water at about 100°, a sticky, almost gelatinous substance, insoluble in cold spirit and behaving like gelatin towards reagents (v. Bibra). Human hair heated with water to a moderately high temperature in a Papin's digester, dissolves almost entirely with evolution of sulphuretted hydrogen. The solution gives abundant precipitates with chlorine and tincture of galls, and with strong mineral acids, and leaves a sticky mass when evaporated. At a higher temperature in the digester, ammonia and empyreumatic oil are produced (Vauquelin). Hair evolves sulphuretted hydrogen even on prolonged boiling with water, colours the water yellow, and gives up to it a substance precipitable by tannic acid and neutral acetate of lead. It retains its form even after prolonged boiling under a pressure of 8½ atmospheres, but gives up to the water a substance which forms a grey deposit and an extract partially soluble in alcohol (v. Laer).

Feathers heated to 200° with water for some hours dissolve to a yellow liquid, which smells of burning feathers, and deposits flocks (Leyer & Köller). Quills also dissolve in a Papin's digester (Bogdanow, *Compt. rend.* 45, 688).

Hair turns yellowish in *chlorine*, and softens to a sticky mass (Vauquelin). Van Laer obtained proteinchlorous acid (p. 265). — Hair, wool, and horn, treated with *sulphuric acid* and *binoxide of manganese*, or *bichromate of potash*, yield benzoic acid amongst other products (Vohl, *Chem. Centr.* 1868, 71).

Horn substance colours dilute *nitric acid* yellow, and is converted by prolonged treatment into a yellow mass, which, after washing with cold water, dissolves to a yellow gelatinous liquid in boiling water. Strong nitric acid dissolves horn rapidly, with evolution of nitric oxide (Hatschett). Hair treated with nitric acid yields xanthoproteic acid, then a reddish-brown solution containing sulphuric, oxalic, and saccharic acids (v. Laer). Cows' horns and horses' hoofs likewise yield xanthoproteic acid (Van der Pant, *Kopp's Jahresber.* 1849, 507).

Horn boiled with moderately dilute *sulphuric acid*, yields leucine and tyrosine (Hinterberger); also aspartic acid (Kreusler, *J. pr. Chem.* 107, 240).

Goose feathers swell up to a gelatinous mass in dilute sulphuric acid, and on prolonged boiling therewith, dissolve to a dark-brown liquid, which evolves ammonia and an odour of volatile bases when neutralised with lime, and contains a body precipitable by neutral acetate of lead. Human hair and hedgehog's spines yield the same products (Leyer & Koller, *Ann. Pharm.* 83, 332).

When serpent's skin is treated alternately with cold oil of vitriol and cold potash-ley, whereby nitrogenous substances are dissolved, there remains a substance which is isomeric with cellulose, and yields fermentable sugar on boiling with dilute acids (De Lucca, *Compt. rend.* 57, 437). See also xv, 309.

Hydrochloric acid acquires a brown colour by long contact with horn-substance, horn itself assuming either a dark-blue or a brownish purple-red colour, which is changed to dark-yellow by nitric acid, and to orange by ammonia (Hatschett). Hair dissolves in hydrochloric acid after long boiling, with formation, according to v. Laer, of humic acid and sal-ammoniac.

Hot aqueous *potash* dissolves horn-substance, with evolution of ammonia; the solution gives with acids a precipitate soluble in excess of acid (Hatschett, *Scher. J.* 6, 301). The alkaline solution contains acetic acid, and evolves sulphuretted hydrogen with acids. When it is precipitated in two portions by acetic acid, the first grey precipitate contains more carbon than the second yellowish-white one (Scherer).

	1. *Precipitate from Horn.*	*Precipitates from Hair.* 1.	2.
C	54·70	54·26	52·84
N	15·59	15·73	14·84
H	7·24	7·16	7·06

According to v. Laer, the first precipitate is Mulder's protein, while that produced by more acid is bioxyprotein. With dilute potash-ley but little bioxyprotein and less protein are obtained (v. Laer). v. Bibra found both precipitates to contain sulphur (1·21 and 1·06 per cent.).

a. Bioxyprotein is pale-yellow while moist, black and resinous after drying. It is insoluble in cold water, but is converted into a sticky mass and partly dissolved by boiling water. Its solution in oil of vitriol is precipitated by water, and that in aqueous alkalis by acids. Insoluble in alcohol. Contains 52·73 p.c. C., 7·04 H., 14·51 N, and 25·72 O.; according to v. Laer $C^{40}N^{5}H^{31}O^{15}$.

b. On passing chlorine into the solution freed from protein by neutralisation with hydrochloric acid, proteinchlorous acid is first thrown down, and afterwards the compound $C^{40}N^{4}H^{31}O^{17},ClO^{3}$ is precipitated. The compound is whitish-yellow, translucent after drying, smells of chlorous acid, and is insoluble in cold water. Boiling water separates a white adhesive mass soluble in acetic acid. The compound dissolves in nitric acid without coloration; in ammonia and potash, from which it is precipitated by dilute sulphuric acid; partially in weak spirit, and completely in absolute alcohol (v. Laer).

When horn-shavings are fused with *hydrate of potash* till hydrogen and ammonia are evolved, leucine and tyrosine are formed, together with acetic, butyric, and valerianic acids (Hinterberger).

Horn-substance swells up in *acetic acid* without undergoing any essential alteration in structure, and dissolves in the liquid on boiling. — Hair colours strong acetic acid yellow, and becomes brittle (v. Laer). — Hair freed from fat by ether-alcohol, nails, hedgehog's spines, the scales of *Coluber natrix*, as well as the non-albuminous elastic fibres of the aorta of the ox, dissolve almost entirely in glacial acetic acid at

120°, forming brown solutions. The solution of hair contains hydrosulphuric acid, the other solutions do not. The acetic solution is rendered turbid by water, and is abundantly precipitated by caustic soda and its carbonate, the precipitate from the solution of hair being soluble, and that from solution of elastic fibres insoluble, in excess of soda-ley (G. Judell, *Tubinger medic. Unters.* 1, 438).

The *epithelium of the mucous membrane* of whalebone, scraped off and washed with water, alcohol, and ether, is triturable to a yellowish-white dusty powder, which dissolves with dark-blue colour in boiling hydrochloric acid, and is slightly soluble in acetic acid. Its alkaline solution gives with acetic acid a precipitate soluble in excess of acid, this last solution being precipitated by ferrocyanide of potassium (Gorup-Besanez, *Ann. Pharm.* 61, 49). See the analysis, p. 348.

When dry *sheep's wool* is treated with anhydrous ether, cold water, alcohol, and hydrochloric acid containing 0·13 p. c. in succession, and then again exhausted with alcohol and ether, the wool-fibre is left free from soluble constituents, and containing only such impurities as may be removed mechanically. In this process the ether takes up fat, the water takes up sweat, and the other liquids take up small quantities of soap. The purified fibre amounts to 20 to 50 p. c. of the air-dried wool (Märcker & E. Schulze, *J. pr. Chem.* 108, 193).

Analyses of Wool-fibre, ash being deducted.

			Märcker & Schulze.		
	Scherer.	Ulbricht.	*mean.*	*max.*	*min.*
C	49·86	50·48	49 54	50 46	49·25
H	17·71		15·60	16·08	15·54
N	7·03	7·00	7·29	7·58	7·19
S		2·85—3·84	3 44	3·73	3 41
Ash	2 0	0 06—0·29	0·15	0·37	0·08

Scherer (*Ann. Pharm.* 40, 53). Ulbricht (*Annalen der Landwirthschaft,* 49, 138).

Wool contains 1·78 p. c. of sulphur (Chevreul); 0·8 to 0·9 p. c. (v. Bibra). Sheep's wool dried at 100°, contains 1·3 to 3·4, on the average 2·31 p. c. of sulphur, of which it gives up none on boiling with distilled *water*. Spring or river water takes up a part of the sulphur on boiling, on account of the presence of alkaline salts (Grothe). Sp. gr. 1·614 (Grassi, *Kopp's Jahresber.* 1847 and 1848, 39). Wool turns yellow at 130°, curling up and emitting an odour. At higher temperatures it assumes a golden-brown colour, the scales being darker than the cell-contents (Grothe). When submitted to dry distillation, it yields a stinking oil, a large quantity of hydrosulphuric acid, also pyrrol, sulphide of carbon, and carbonate of ammonia, with traces of volatile bases (Williams).

Wool is less readily attacked by *nitric acid* than silk (Barreswil, *N. J. Pharm.* 32, 123). It yields with nitric acid xanthoproteic acid (van der Pant, *Jahresber.* 1849, 508), but no picric acid (Liebig). It is less easily acted upon than cotton-wool and linen by concentrated sulphuric acid: when a mixture of the fibres is exposed to the action of the acid for 10 or 15 minutes, the cotton or linen is dissolved and may be washed away, without the wool being acted upon (Böttger, *J. pr. Chem.* 73, 498). When 1 part of woollen cloth is moistened with 4 parts of oil of vitriol and 1 part of water, it assumes a reddish colour and evolves a small quantity of sulphurous acid: if it be then gently warmed, it forms first a homogeneous jelly and then a red solution, which when diluted, boiled for some time, neutralised with lime, and evaporated, leaves a yellowish extract. This body contains ammonia-salt, a little leucine, a substance poor in nitrogen and soluble in alcohol, and another body insoluble in alcohol, the latter being precipitable by basic acetate of lead, mercurous nitrate, and tannic acid. By the less prolonged action of sulphuric acid, a body richer in nitrogen is formed, also insoluble in alcohol, and externally resembling glue (Braconnot, *Ann. Chim. Phys.* 12, 186; 13, 121).

Wool dissolves in hot aqueous *potash*, evolving ammonia and turning brown. The solution, when mixed with hydrochloric acid, gives off hydrosulphuric acid, and deposits a brown pitchy precipitate, containing sulphur and nitrogen, whilst an amorphous body, likewise containing sulphur and nitrogen, and soluble in alcohol, remains in solution (Braconnot, *Ann. Chim. Phys.* 93, 268). Aqueous solutions of caustic alkalis and of carbonate of soda or ammonia, extract from wool a part of the sulphur, but not the whole, even when boiled with it as long as sulphide continues to be formed. The precipitate produced by acetic acid in alkaline solutions of wool also contains sulphur (Grothe, *J. pr. Chem.* 89, 420). The alkaline solution, when evaporated and distilled, yields amylamine and butylamine (Gr. Williams, *Chem. Gaz.* 1858, 380; *Ann. Pharm.* 109, 127).

When wool which has been treated with *potash* is steeped in solution of *cupric sulphate*, it afterwards assumes a bronze colour in the air, due to sulphide of copper (Grothe, *Anal. Zeitschr.* 3, 153).

Ammoniacal solution of oxide of copper dissolves wool completely only when warmed (Schwezer, *J. pr. Chem.* 72, 109). It does not dissolve wool in the cold (Stefanelli, *Dingl.* 156, 225), even in 14 days (Ozonam, *Compt. rend.* 55, 863). — *Chloride of zinc* does not colour wool at 130° to 150° (Maumené, *Compt. rend.* 30, 447). — Wool acquires a permanent yellow colour in dilute *picric acid* (Pohl, *Wien. Acad. Ber.* 9, 386; *Jahresber.* 1852, 825).

Ossein.

FREMY. *N. Ann. Chim. Phys.* 43, 51; *N. J. Pharm.* 27, 1; *Jahresber.* 1854, 700.

The organic basis of bone. Occurs also in reindeer's feet, stag's horns, and whalebone. On allied substances, see below.

Bones are treated repeatedly with a mixture of 1 part of hydrochloric acid and 9 parts of water; after some days the residue, which has become translucent and elastic, is washed with cold and warm water so long as it gives up hydrochloric acid, and until a portion of it gives with boiling water a solution of gelatin free from chlorine. The product is further washed with alkaline water, alcohol, and ether. Ossein thus obtained still contains traces of ash and small quantities of blood-vessels, which remain undissolved on treating it with boiling water.

Ossein contains 50·4 p.c. C., 16·9 N., 6·5 H., and 26·2 O. In boiling water it is very slowly converted into an equal weight of gelatin; more rapidly when prepared from the bones of young animals; and very speedily after addition of small quantities of acid.

Fish-bones and the bones of *water-birds* contain, besides ossein, a substance soluble in boiling water and having, apparently, the same composition. When these bones are freed from lime-salts by means of cold dilute hydrochloric acid and the residue is washed free from acid and then boiled with water, the ossein dissolves as gelatin, whilst a transparent elastic residue, having the form of the bones, remains undissolved (Fremy).

The substance corresponding to ossein in the *tortoise* contains as much as 2 p .c. of sulphur, 53·45 p. c. C., 16·35 N., 7·25 H., and 22·95 O. It is very slowly altered by boiling water and acids (Frémy).

Glutin or Bone-gelatin.

HATSCHETT. *Phil. Trans.* 1800, 369; *Scher. J.* 6, 290.—BOSTOCK. *N. Gehl.* 4, 552.—JOHN. *Schw.* 15, 200.—BRACONNOT. *Ann. Chim. Phys.* 13, 113; *Schw.* 29, 344.

J. MÜLLER. *Pogg.* 38, 295.

J. G. MULDER. *Pogg.* 40, 279; *Berzel. Jahresber.* 18, 640.—*Bulletin en Neerlande,* 1, 23; *Berzel. Jahresber.* 19, 721.—*Scheik. Onderz.* 1, 67; *Berzel. Jahresber.* 23, 683.—*Ann. Pharm.* 46, 205; *Berzel. Jahresber.* 24, 711.

VAN GOUDOEVER. *Scheik. Onderz.* 3, 251: *Ann. Pharm.* 45, 62,; *Berzel. Jahresber.* 23, 681.

Animal gelatin. Glue.—Formed from the gelatigenous tissues, that is to say, from the intercellular substance (the filaments) of the true connective tissue of sinews, ligaments, fascia, bones after ossification, whalebone, and teeth, by boiling with water.

According to J. Müller, fibro-cartilage yields glutin, but according to Mulder (*Physiol. Chemie,* 603) and Hoppe-Seyler, it yields chondrin (See *Handbuch,* viii, 454; *Lehmann's Physiological Chemistry,* iii, 40, 42). The gelatin of elastic tissue exhibits some peculiar reactions (J. Müller). See *Handbuch,* viii, 453.

Chevreul (*Ann. Chim. Phys.* 19, 33; *Gilb.* 70, 375) observed that tendons dried at 100°, when converted into gelatin by boiling with water, yielded an equal weight of gelatin dried at 100°, and hence concluded that gelatigenous tissues and gelatin have the same composition. This was also shown by Scherer's analyses of connective tissue (*Handbuch,* viii, 458; *Lehmann's Physiol. Chem.* iii. 47) and by Fremy's analyses of ossein (p. 352) and gelatin. Chevreul's observation has recently been confirmed by De Bary in the case of isinglass.

Preparation. Bones broken up and washed are treated with hydrochloric acid of sp. gr. 1·04, whereby the phosphates and carbonates are removed; and the residual bone-cartilage is washed and converted into gelatin by boiling it for six or eight hours with water. The solution, clarified by standing in moderately warm vessels, and poured upon slate or stone slabs, solidifies as it cools; the plates of gelatin may then be cut up and dried, first in the air and afterwards in a drying-closet. A less pure gelatin is obtained by boiling comminuted bones with water, without previous treatment with hydrochloric acid. Other materials employed for the preparation of pure gelatin are isinglass and stag's horns.

Connective tissue contains, besides the gelatigenous fibrillæ, cementing substance, elastic fibres, and corpuscles, the removal of which may be effected approximately as follows. Tendons are cut into very thin slices, which are treated with fresh portions of water so long as they give up albuminates; the residue is digested for several days with a large quantity of lime- or baryta-water in closed vessels, whereby the cementing substance is dissolved; the swollen residue is washed, first with water and then with acetic acid, so dilute that the substance shrinks together but does not again swell therein, and lastly exhausted with water. The remaining fibrillæ still contain that portion of the corpuscles which is insoluble in water and dilute alkalis; when submitted to prolonged boiling with water, or when heated to 120° in a Papin's digester, they yield a solution of gelatin in which ferrocyanide of potassium reveals the presence of a little syntonin (*Kühne's Physiol. Chemie*, 355).

Gelatin from isinglass may be purified by solution in hydrochloric acid and dialysis; there remains on the dialyser a jelly which is free from ash-constituents and does not putrefy (Graham, *Ann. Pharm.* 121, 1).

Glue is prepared from the hides of animals. The offal of hides is left for two months or so in milk of lime frequently renewed, and then washed with water, by which operations hair and adhering portions of flesh, blood, and fat are removed. After exposure to the air for some days, to convert adhering lime into carbonate, the whole is boiled with a sufficient quantity of water till complete solution is effected. The solution of glue thus obtained is clarified by deposition, then run into suitable vessels, in which it solidifies on cooling, and lastly cut up and dried.

Gelatin may be obtained from thin leather (upper leather) by boiling it with lime and water in a Papin's digester; sole-leather and old long kept leather cannot be converted into gelatin in this way (Stenhouse, *Ann. Pharm.* 104, 239).

Properties. Colourless or yellowish, transparent or translucent, horny, elastic mass, brittle and of conchoïdal fracture. Heavier than water; tasteless and inodorous; without action on vegetable colours. — Rotates a ray of polarised light to the left: the rotatory power is reduced by warming or by the addition of soda-ley, but not by the addition of ammonia (De Bary, *Tubinger medic. Unters.* 1, 73).

			Mulder.		Gondoever.	Frémy.
Calculation according to Mulder.			*a.*	*b.*	*c.*	*d.*
26 C	156	50 00	49·31	50·03	49·22	50·0
4 N	56	17·95	18·37	18·31		17·5
20 H	20	6·41	6·55	6 64	6·72	6·5
10 O	80	25·64	25·77	25·02		26·0
$C^{26}N^4H^{20}O^{10}$	312	100·00	100·00	100·00		100·0
Ash			5·41	0·64		

a was prepared from stag's horn, *b* and *c* from isinglass, *d* from bones. — Gelatin contains neither sulphur nor phosphorus: Schlieper (*Ann. Pharm.* 58, 378), however, found 0·56 p. c. of sulphur in isinglass, and 0·125 p. c. in bones free from sulphuric acid and exhausted with ether. — According to Goudoever, gelatin dried at 100° loses 1·65 p. c. of water at 120°. — When dried with oxide of lead it does not lose any combined water (Mulder).

Neither the above formula of Mulder, nor Liebig's earlier formula, $C^{52}N^8H^{40}O^{20}$, nor yet that proposed by Hunt ($C^{24}N^4H^{20}O^8$) (*Compt. chim.* 1850, 317; *Lieb. Kopp's Jahresber.* 1847 and 1848, 845) can be regarded as established.

Decompositions. 1. Aqueous glutin or gelatin-jelly readily *putrefies*, the jelly becoming fluid and evolving a disgusting ammoniacal odour. Addition of carbolic acid prevents putrefaction (*Oesterr. Vereinszeitschr.* 1868, 477).—2. On prolonged boiling with *water*, the agglutinating power of gelatin and its property of solidifying to a jelly is diminished, and conversely its solubility in cold water is increased. A solution of isinglass in hot water, when exposed to the boiling heat for some weeks in a sealed tube and then evaporated, leaves a hygroscopic brown turpentine-like residue, which dissolves easily in cold *water* and is only partially precipitated by alcohol. The portion thus precipitated does not yield a jelly with water (Gmelin). This change takes place almost instantaneously at 140°, even in presence of only a very small quantity of water: at lower temperatures much more water is necessary, but very dilute solutions of gelatin lose the property of solidifying only after being heated to 50° for twelve hours (Kühne, *Lehrbuch. der Phys. Chemie.* 356).—Glue boiled with water for 55 hours, and no longer capable of gelatinising contains, at 120°, 48·85 p. c. C., 6·56 H., and 17·36 N.; when boiled with water for 100 hours, exhausted with alcohol, and dried at 120°, it contains 49·18 p. c. C., 6·74 H., the composition in both cases corresponding to the formula $2C^{26}N^{4}H^{20}O^{10} + aq.$ (Goudoever).—3. Gelatin submitted to *dry distillation* yields the products mentioned on page 256.—4. In the *fire* gelatin softens, swells up, evolves vapours smelling of burnt feathers, and burns with slight flame.

5. Aqueous glutin mixed with a little potash-ley absorbs *ozonized air* passed into it, acquires a transient violet-red colour, and when afterwards neutralised with sulphuric acid and evaporated, leaves, besides sulphate of potash, a brown amorphous extract, which burns with the odour of horn, is precipitated in amorphous yellow flocks by alcohol, and contains neither glutin, chondrin, nor albuminates (Gorup-Besanez, *Ann. Pharm.* 125, 220.) In the absence of potash gelatin is not attacked by ozone (Gorup-Besanez, *Ann. Pharm.* 110, 102). Contrary to Schönbein's statement (*Ann. Pharm.* 89, 294).

6. When 2 parts of gelatin are heated in a retort with 8 parts of *bichromate of potash*, 15 parts of *oil of vitriol*, and 50 parts of water, till the mixture begins to froth, an acid turbid distillate is obtained, containing hydrocyanic, formic, acetic, valerianic, and benzoic acids, valeronitrile (xi, 121) and valeracetonitrile (xi, 123), and, lastly, a thick colourless oil, smelling of cinnamon (Schlieper, *Ann. Pharm.* 59, 1). Guckelberger (*Ann. Pharm.* 64, 39) obtained the same products as from casein (p. 311), but gelatin yielded a relatively large quantity of formic and valerianic acids and but little oil of bitter almonds. Fröhde (*J. pr. Chem.* 79, 303; 80, 344; *Kopp's Jahresber.* 1860, 568) obtained also acetonitrile and propionitrile: the oil smelling of cinnamon, when exposed to the air or boiled with potash was converted into Fröhde's collinic acid, $C^{12}H^{4}O^{4}$. The production of hydrocyanic acid was previously observed by Persoz (*Compt. rend.* 13, 141; *J. pr. Chem.* 26, 53).—Gelatin behaves like casein also when oxidised with *binoxide of manganese* and *sulphuric acid*, except that little or no propionic aldehyde is formed (Guckelberger).

7. *Chlorine gas*, passed into a solution of gelatin in water, precipitates it completely in white, flexible, tough threads, which evolve

chlorine when heated or when treated with oil of vitriol, and dissolve in alkalis with formation of metallic chlorides, and in hot nitric or acetic acid, from which they are deposited on cooling, but are insoluble in boiling water and alcohol (Thénard, *Mém. d'Arcueil*, 2, 38). When chlorine is passed into a solution of gelatin, the gas-bubbles become covered with a white froth, which collects in flocks on the surface of the liquid: the liquid, which appears milky at first, afterwards deposits a semi-transparent jelly, and then contains hydrochloric acid. *a.* The precipitated jelly contains 80·3 p. c. of gelatin and 19·7 p. c. ClO^3. — *b.* The floating flocks are white and tough, and contain, in the moist state, 75 p. c. of gelatin and 25 p. c. ClO^3. They give off a large quantity of chlorous acid at ordinary temperatures and turn brown at 100°. When dried, first at 30° to 40° and then at 100°, they are converted into a white, inodorous, friable mass of constant composition (see below), insoluble in water and alcohol. Their solution in ammonia evolves nitrogen, and when evaporated leaves sal-ammoniac and gelatin, the latter still having the composition and properties of the gelatin originally employed (Mulder, *Bullet. en Neerlande*, 1839, 153; *Berzel. Jahresber.* 19, 729).

Mulder (C = 75 54).

C	46·66	46·25
N.	15·59	
H	5·90	5·81
O.	23·37	
ClO^3	8·48	8·47

From fish-gelatin, whether boiled with water for 55 or for 100 hours, Mulder & van Goudoever obtained, by treating it with chlorine, a compound containing, at 110°, 43·16 p. c. C., 5·65 H., and 13·23 ClO^3. See also Mulder (*Ann. Pharm.* 46, 205; *Berzel. Jahresber.* 24, 711).

8. When 1 part of gelatin in powder is mixed with 2 parts of *oil of vitriol*, the mixture remains uncoloured for 24 hours: on now adding 8 parts of water and boiling for 5 hours, the water evaporated being replaced, glycogen, leucine, a body poor in nitrogen, and precipitable by tannic acid, and an ammonia-salt are formed (Braconnot). Fish-gelatin, boiled for some days with dilute sulphuric acid, yields sulphate of ammonia and fermentable sugar (Gerhardt, *Traité*, 4, 509). — 8. Fuming *nitric acid* dissolves gelatin, with evolution of nitrogen, a little nitric oxide, and carbonic acid, and formation of oxalic and malic acids and fat (Scheele). Very weak nitric acid dissolves gelatin without evolution of nitric oxide, forming a yellow liquid which explodes when evaporated (Hatschett). Gelatin heated with an equal weight of water and one-fifth of nitric acid till it effervesces, and then cooled, forms Dumoulin's fluid gelatin (*Compt. rend.* 35, 444; *J. pr. Chem.* 58, 59). — Gelatin is not decomposed by boiling with aqueous *iodic acid* (Millon).

9. Other acids act like nitric acid in depriving gelatin of its property of gelatinising on cooling. *a.* Strong acetic acid dissolves gelatin softened in water, and destroys its property of gelatinising, but not its agglutinating power on drying. — *b.* When gelatin is allowed to swell in cold aqueous oxalic acid, and cautiously warmed till the mass remains fluid on cooling, then shaken with carbonate of lime to remove oxalic acid, and filtered, a neutral tasteless solution is obtained

which does not readily undergo putrefaction. It forms Carey Lea's *metagelatin.*

10. Gelatin boiled with *potash-ley* yields a large quantity of glycine and less leucine (Mulder, *J. pr. Chem.* 16, 290).—Heated with *potassium* or *sodium*, it oxidises slowly and carbonises without evolution of light (Gay-Lussac & Thénard).

11. A piece of gelatin placed in acid *mercuric nitrate* gradually turns red and dissolves to a fine red liquid, which becomes darker when boiled, and is turned dirty-yellow by chlorate of potash. *Mercurous nitrate* dissolves gelatin with yellow colour on boiling. Metagelatin behaves in a similar manner (Carey Lea, *Sill. Amer. J.* [2] 40, 81; *J. pr. Chem.* 97, 58). Nicklès (*J. Pharm.* [4] 3, 152) believes the red colour to be due to adhering albumin. See p. 262.

Combinations. Gelatin prepared from the skins of old animals swells up in water to a soft, sticky, translucent mass, without dissolving to any great extent: that prepared from the skins of younger animals, or from feet, sinews, or isinglass, dissolves partially or entirely in a larger quantity of cold water. With warm water it rapidly forms a perfect solution, which solidifies to a transparent jelly on cooling, provided it contains at least $\frac{1}{150}$th of gelatin.—The solidification of very dilute solutions of gelatin is prevented by vigorous and prolonged shaking, the cold solution then forming a syrup (Kühne). Isinglass gelatin retains its solubility in hot water after boiling with alcohol and drying at 125°: gelatin from stag's horn is not soluble after being thus treated (Mulder).

Hydrochloric, *acetic*, and other *dilute acids* dissolve gelatin without decomposition (Hatschett), and produce no precipitate in its aqueous solution (J. Muller). When added in very small quantity to water, they effect the dissolution of gelatin, even in the cold (Kühne). Solutions of gelatin are precipitated by *hydriodic acid*, but not by *iodine* or *iodic acid* (Vauquelin).

Gelatin purified by Graham's process of dialysis, combines with colloïd acids, and was hence termed by Graham a colloïd base. Thus, on dropping *metasphosphoric acid* into aqueous gelatin, a semitransparent, soft, elastic mass is thrown down, resembling fibrin, and containing 3·6 parts of acid to 100 of gelatin (Graham).

Graham's colloïd *silica* throws down from excess of aqueous gelatin white flocks which are not decomposed by washing do not putrefy, and contain 100 parts of silica to about 92 parts of gelatin. On adding gelatin-solution to excess of silica, a compound of 100 parts of silica with 56 parts of gelatin is obtained (Graham, *Chem. Soc. J.* xv, 246; *Ann. Pharm.* 121, 40).

Hot aqueous *potash* and *soda* dissolve gelatin, without evolution of ammonia, forming a brown liquid not precipitable by acids (Hatschett). *caustic lime* and *phosphate of lime* dissolve in aqueous gelatin (Vauquelin, *J. Phys.* 85, 127).

Gelatin is not precipitated by *alum*, or by a mixture of alum and salt (J. Muller). Alum containing alkali throws down a compound of gelatin with basic sulphate of alumina.—*Chloride of zirconium* likewise precipitates gelatin (Berzelius).

Gelatin forms with aqueous *chromic acid* a dark-yellow coagulum, which dissolves on heating (Hünefeld, *J. pr. Chem.* 9, 30). Solution of gelatin mixed with chromate of potash is converted into an insoluble yellow mass by exposure to light.

Aqueous gelatin forms with *protochloride of tin* large brown flocks (Gmelin), and yields ammonia when digested with bichloride of tin (Schenk & Chapman, *Laboratory* i, 152; *Chem. Centr.* 1868, 311). It does not precipitate *neutral acetate of lead* (J. Müller), but produces a turbidity in the *basic acetate*, and after some hours solidifies with it in a white mass (Gmelin). According to Heintz (*Zoochemie*, 747), it is not precipitated by basic acetate of lead.

Solution of gelatin does not precipitate *ferric sulphate;* common glue produces therewith, after standing for some time, a precipitate which dissolves on warming (J. Müller). Strong solution of isinglass forms with ferric sulphate a jelly, which dissolves when moderately heated, and deposits reddish-yellow flocks on boiling. These flocks contain, at 120°, 44·65 to 48·51 p.c. ferric oxide, and 11·96 to 11·85 SO^3 (Mulder).

Gelatin mixed with potash-ley dissolves *cupric hydrate* with violet colour (Lassaigne, *J. Chim. méd.* 18, 260). When mixed with *cupric sulphate*, it forms a clear green liquid, which is turned violet by caustic potash, and from which the copper cannot be precipitated, or only in combination with organic substance (Mitscherlich, *Pogg.* 40, 129). The alkaline solution turns pale-red when boiled, without depositing cuprous oxide (Hoppe-Seyler). See p. 262.

According to John, Orfila, and others, aqueous gelatin precipitates *mercuric chloride* in white curdy flocks, which, according to J. F. Simon, *Pogg.* 40, 311) are soluble in excess of gelatin, and, according to Orfila, dissolve on heating. The precipitate is tenacious, and not susceptible of filtration (Kühne).

Solution of gelatin precipitates *terchloride of gold* when not too dilute (Bostock); according to Ed. Davy (*Schw.* 31, 350) and J. Müller it produces a brown tenacious precipitate with *platinic sulphate*, and, according to Gmelin and J. Müller, yellowish-white flocks with *platinic chloride*, after which complete coagulation ensues. It precipitates *chloride of iridium* (Chevreul).—Acidified bone-gelatin produces with *platino-cyanide of potassium* a thick precipitate, which deliquesces to a viscid liquid, puffs up like sulphocyanate of mercury when burnt, and leaves charcoal (Schwarzenbach, *Ann. Pharm.* 133, 193).

Gelatin is insoluble in *alcohol*, *ether*, *volatile* oils and *fat oils*, and is precipitated from its aqueous solution by alcohol. Gelatin from isinglass dissolves more easily than ordinary gelatin in weak spirit (J. Muller).

Aqueous gelatin is precipitated by *carbolic acid* (Graham); by *hæmatoxylin* (xvi, 292), especially in presence of an acid (Chevreul); by a mixture of *gallic acid* and *gum* (Pelletier). Its solutions are not precipitated by gum arabic or arabate of potash, but *arabic acid* purified by Graham's process of dialysis precipitates gelatin similarly purified, in oily drops which solidify to a nearly colourless jelly on standing, and liquefy again at 25°. The jelly may be washed without decomposition, but dissolves slightly in pure water, and more freely in solution of gelatin. It contains 83·5 p.c. of water, and, when prepared with excess of arabic acid, 100 parts of arabic acid to 59 parts of gelatin (Graham, *Chem. Soc. J.*, 15, 258; *Ann. Pharm.* 121, 56).

Tannic acid produces, with gelatin, a white opaque precipitate, which, when the gelatin is in excess, dissolves on warming, but when the tannic acid predominates, does not dissolve, but forms a grey very elastic pellicle. In both cases the filtrate is turned blue by ferric salts (Pelouze, *J. Chim. méd.* 10, 261). The brown, tough, flexible substance formed with tannic acid and gelatin is not susceptible of putrefaction; it is soluble in alkalis, and is decomposed by magnesia and by oxide of lead, which take up the tannic acid, so that the gelatin becomes soluble in water (Davy; Löper).

According to Mulder, gelatin forms two compounds with *quercitannic acid*. *a*. When gelatin is added to excess of the acid, 100 parts of gelatin require 134 to 135·6 parts of acid, the precipitate containing 52·34 p. c. C., 3·83 H., and 7·84 N. — *b*. When, on the other hand, the acid is added to excess of gelatin, the precipitate consists of 100 parts of gelatin to 85·2 parts of acid, and contains 51·93 p. c. C., 5·06 H., and 9·63 N. (Mulder).

Chondrin.

J. Müller. *Pogg. Ann.* 38, 295; *Ann. Pharm.* 21, 277; *J. pr. Chem.* 10, 488.
J. G. Mulder. *Natur. a. Scheik. Arch.* 1837, 3, 480; *Berzel. Jahresb.* 19, 722; *Pogg.* 44, 440; *J. pr. Chem.* 15, 190. — *Scheikund. Underzoek.* 1, 68; *Berzel. Jahresb.* 23, 687.
Vogel. Jun. *J. pr. Chem.* 21, 426; *Berzel. Jahresb.* 21, 542.
J. Scherer. *Ann. Pharm.* 40, 49; *Berzel. Jahresb.* 22, 568.
G. D. Schröder. *Ann. Pharm.* 45, 52; *Berzel. Jahresb.* 23, 688.
F. Hoppe. *J. pr. Chem.* 56, 129; *Kopp's Jahresb.* 1853, 695.

Cartilage-gelatin. Knorpelleim. — First distinguished by J. Müller. — Formed from the permanent cartilages, the bone-cartilages before ossification, and the cornea of the eye, by prolonged boiling with water (*Handbuch* viii, 451; *Lehmann's Physiological Chemistry*, i, 398).

Conversion of Chondrin into Glutin. Vogel, and, after him, Friedleben (*Zeitschr. für wissensch. Zoologie von Siebold. u. Kölliker*, 10, 29; *Jahresb.* 1859, 623), observed that hyaline cartilages, after several days' maceration in dilute hydrochloric acid and washing, dissolve when boiled with water for an hour or two, forming a solution which exhibits, not the reactions of chondrin, but, according to Friedleben, those of glutin. M. Willens, however (*Zeitschr. f. wissensch. Zoologie* 10, 467; *Jahresb.* 1860, 392), observed that no conversion of chondrin into glutin takes place under these circumstances. Friedleben's solution does not, indeed, exhibit the reactions of chondrin; neither, however, does it exhibit those of glutin, inasmuch as it does not precipitate infusion of galls, but gives a cloud with neutral acetate of lead, and precipitates the basic acetate. C. Trommer (*Virchow's Arch.* 19, 554; *Jahresb.* 1860, 503) obtained with cartilage which had been treated with dilute acid, the reactions of glutin; but after all the acid had been removed by means of ammonia, the solution exhibited the reactions of chondrin. The supposition that chondrin is converted into glutin is, therefore, inadmissible: neither does any such conversion take place during ossification, but the chondrogenous cartilage is replaced in that process by the osteoïdal connecting substance. See also C. Bruch (*Handbuch*, viii, 457). The same result was obtained by M. Schultze (*J. pr. Chem.* 83, 162). Preliminary treatment of the cartilage with potash-ley at 45—50° altered the reactions of the chondrin, but did not bring them into accordance with those of glutin; in particular, the chondrin of these cartilages was not precipitable by mercuric chloride, although it gave the reactions of glutin with tannic acid, acetic acid, oxalic acid, and alum. By previous treatment of the cartilage with acid, the chondrin lost its capability of being precipitated by acetic acid, oxalic acid, alum, ferrous sulphate, ferric sulphate, and cupric sulphate, but, at the same time, it became unprecipitable by mercuric chloride, and only partially precipitable by tannic acid. For the rest, the reactions of chondrin, as described by M. Schultze, do not agree with those given by J. Müller.

The hyaline cartilage of growing stag's horn yields glutin by six hours' boiling, and if the undissolved portion be further boiled for 20 hours, the solution will contain both glutin and chondrin. Young stag's horn, which had already passed into the stage of ossification, yielded only glutin. Hence it appears that in the process of ossification, the chondrogenous tissue is replaced by a colligenous tissue, although even the full-grown anthers generally contain remains of unmetamorphosed cartilage (Lieberkühn, *Muller's Archiv.* 1862, 702). See also Hoppe (*Virch. Archiv.* 5, 171).

Preparation of Chondrin. Rib-cartilage is boiled with water for half an hour, whereby the enveloping membrane is partly loosened and rolled up, and partly rendered removable with the knife; the cartilages thus purified are comminuted, macerated for several hours in cold water, and boiled for an hour with a sufficient quantity of water under a pressure of two or three atmospheres, whereby the cartilage is for the most part dissolved. The liquid filtered at the boiling heat is evaporated, and the residue, after washing by decantation with cold water, is dried, pulverised, and boiled with alcohol. Chondrin thus prepared contains, on the average, 6·4 p. c. ash (Hoppe).

To obtain chondrin free from ash,—which, however, is very difficult to dissolve in boiling water, the above hot-filtered liquid is precipitated with acetic acid, and the precipitate is washed, dried, and boiled with alcohol.

Vogel boils rib-cartilage with water for 48 hours; Mitscherlich boils it for 24 hours and precipitates with alcohol, whereby the chondrin is obtained as a white tenacious mass.

Properties. Hard and very brittle mass, nearly colourless, transparent, light-brown in thickish layers. Very hygroscopic; gives off the last portion of its water very slowly at 120° (Hoppe); after drying at 100°, it still gives off 2·33 p. c. water at 100° (Schröder).

Lævorotatory. For a solution mixed with a little caustic soda and containing not quite $\frac{1}{10}$ p. c., $[\alpha]\,j = 213{\cdot}5°$; dilution with an equal quantity of water increases the molecular rotation to 281° (J. de Bary, *Tübinger medic. chem. Untersuch.* 1, 71).

	Mulder. *at* 130°.	Scherer. *at* 100°.		Schröder. *at* 120°.
		a.	*b.*	
C	42·27	50·21	49·09	49·36
N	14·50	14·91	14·40	
H	6·63	6·96	7·09	6·61
O	29·60	27·92	29·42	
Ash	6·37	6·6	1·6	8·51

According to Mülder (*Physiol. Chem.* 340) it is $10C^{32}N^{4}H^{20}O^{14} + S$. —Mulder's chondrin contained 0·38 p. c. sulphur. Verdeil (*Ann. Pharm.* 58, 320) estimated the amount of sulphur in cartilage, after deduction of that which is present as sulphuric acid, at 0·654 p. c.; but on the conversion of the cartilage into chondrin, a large quantity of sulphuretted hydrogen was evolved. In chondrin, M. Wilkens (*Zeitschr. für wissenschaftliche Zoologié von Siebold u. Kölliker* 10, 467, *Jahresb.* 1860, 592) found, on the average, 0·518 p. c. sulphur.—Scherer analysed, not ready-formed chondrin, but (*a*) purified rib-cartilage, and (*b*) cornea. — The ash is deducted in every case.

Decompositions. 1. By prolonged boiling with water, chondrin loses the power of forming a jelly on cooling, and then becomes soluble even in cold water, the solution exhibiting the reactions of unaltered chondrin. Still longer boiling produces flocks which dissolve in alkalis, but not in water, alcohol, or ether (Hoppe).—2. By oxidation with *chromic acid* it yields hydrocyanic, but no formic or acetic acid (Hoppe). 3. Chondrin suspended in its own volume of *oil of vitriol* dissolves after some days to a slimy black liquid, which, when diluted and boiled, deposits carbon and yields a brown viscid extract, soluble in alcohol, together with leucine; glycine is not produced (Hoppe). R. Otto (*Zeitschr. f. Chem.* [2], iv, 630) likewise obtained no glycine.—4. *Chlorine gas* passed into aqueous chondrin forms a white precipitate, becoming sea-green and hard when dry, and containing, at 100°, 45·48 p. c. C., 6·09 H., 13·71 N., 7·21 Cl., and 26·88 O., therefore $C^{32}N^{4}H^{26}O^{14}Cl$; when treated with alkalis, it yields unaltered chondrin (Schröder). — 5. When rib-cartilage, purified with dilute hydrochloric acid, is boiled with fuming *hydrochloric acid*, fermentable sugar is formed (G. Fischer & Boedeker, *Ann. Pharm.* 117, 111). See also Schiff (*Ann. Pharm.* 119, 256). The sugar prepared from chondrin is lævorotatory, and differs both from dextrogluose and from lævoglucose (De Bary). Boedeker (*Schmidt's Jahrb. d. Ges. Medic.* 90, 150) formerly described this sugar as *chondroïtic acid.* — 6. Chondrin fused with 2 pts. *potash-hydrate* produces a large quantity of oxalic acid, a small quantity of leucine, and a non-volatile organic acid, which forms a crystalline lime-salt. Concentrated aqueous alkali dissolves chondrin, with violent evolution of ammonia, which soon slackens when the liquid is boiled, but does not cease entirely till some time after; the solution yields a syrupy extract, together with glycine. Dilute aqueous alkalis prevent the formation of the chondrin-jelly, and gradually decompose it, with evolution of ammonia, without forming glutin (Hoppe).— Glycine is not formed by boiling chondrin with *baryta-hydrate* (R. Otto).

Combinations. Dried chondrin swells up in cold *water* to between 11 and 12 times its volume, forming an opaque mass; in boiling water it dissolves more slowly than glutin, and the solution solidifies to a jelly on cooling (Hoppe). Chondrin recently precipitated by alcohol dissolves in cold water (Mitscherlich).

From aqueous chondrin *acetic acid* and most other *acids* throw down precipitates; that formed by acetic acid is not soluble in excess (J. Müller; Vogel).

Carbonic acid, passed into aqueous chondrin, produces at first transient, then permanent flocks, which dissolve in ammonia, but not in hydrochloric acid; all the chondrin is ultimately precipitated. The precipitate deliquesces, when heated or left on the filter, to a viscid liquid which reacts like dissolved chondrin. It gives off carbonic acid when treated with hydrochloric acid, and is, therefore, probably a loose combination of carbonic acid and chondrin (Vogel).

Phosphorous acid and *phosphoric acid* throw down from solution of chondrin a precipitate soluble in excess of the acid; *pyrophosphoric acid* also precipitates chondrin, but does not redissolve it. — The precipitate formed by a very small quantity of *sulphuric acid* dissolves in the smallest excess (Vogel). Warm aqueous chondrin becomes milky when *sulphurous acid* is passed through it, and deposits chondrin as a glutinous precipitate; by prolonged action of the acid decomposition takes place, attended with the formation of ammoniacal salts (Hoppe).

Hydrochloric, *hydriodic*, and *nitric acid* precipitate and redissolve chondrin (Vogel). *Nitrous acid* precipitates a solution of chondrin, and afterwards forms xanthoproteic acid (Hoppe). *Arsenic acid* precipitates but does not redissolve it (Vogel).

The precipitate formed in a chondrin solution by *acetic acid* is fine-grained, insoluble even in a large excess of acetic acid, but soluble in carbonate of potash, also in a large quantity of common salt, acetate of potash, or acetate of soda (Muller). The precipitate is free from acetic acid; and consists of microscopic transparent spherules, which melt when the liquid is boiled, adhere in the form of jelly to the sides of the vessel, and may then be separated from the liquid (Hoppe). Oxalic, lactic, tartaric, and other organic acids react like acetic acid (Vogel; Hoppe).

Alum and *sulphate of alumina* precipitate aqueous chondrin completely in dense white flocks, which easily cake together, are insoluble in hot water, but dissolve in excess of the precipitant, also in a large quantity of common salt or of an alkaline acetate (J. Müller). — *Neutral acetate of lead* forms a precipitate insoluble in excess (Müller).

The precipitate formed by *ferric sulphate* is insoluble in excess of the precipitant, but dissolves when the liquid is heated. It contains at 120°, 6·81 to 8·10 p. c. Fe^2O^3, 5·48 SO^3, 87·07 chondrin (Mulder).

From excess of aqueous *cupric sulphate*, chondrin throws down a precipitate which disappears on agitation; the green precipitate formed on dropping cupric sulphate into aqueous chondrin dissolves at first on agitation, and does not become permanent till a larger quantity of cupric sulphate is added. It is then soluble in hydrochloric, but not in acetic acid. Both the solution and the precipitate exhibit towards reagents a behaviour different from that of cupric solutions in general, so that the copper cannot be detected till the organic substance has been destroyed (Mitscherlich, *Pogg.* 40, 129).

Aqueous chondrin is precipitated by *mercuric chloride* and *infusion of galls*, but not by *silver nitrate*. — The hydrochloric acid solution is not precipitated by *ferricyanide of potassium* (Müller). — *Quercitannic acid* produces a precipitate not separable by filtration (Mulder).

Chondrin is precipitated by *alcohol* in dense white threads (Mulder).

Fibroïn.

ROARD. *Ann. Chim.* 65, 44.
MULDER. *Pogg.* 37, 594; 39, 498; 40, 289.
STÄDELER. *Ann. Pharm.* 111, 12; *J. pr. Chem.* 78, 169; *Chem. Centr.* 1859, 705; *N. J. Pharm.* 36, 229; *Repert. Chim. pure*, 1, 569; *Jahresber.* 1859, 598.
A. VOGEL, jun. *N. Repert.* 8, 1; *Chem. Centr.* 1859, 527; *Jahresber.* 1859, 598.
E. CRAMER. *Unters. der Seide u. des thierischen Schleims*, Zürich, 1863; *J. pr. Chem.* 96, 76; *Chem. Centr.* 1866, 1; *Jahresber.* 1864, 628; 1865, 653. — *Züricher Vierteljahrschrift*, 9.
BOLLEY. *J. pr. Chem.* 108, 364.

Seidenstoff. Seidenfaserstoff. Seidenfibrin. — *Sericin* (Schlossberger).

Occurrence. In silk. White raw silk contains fibroïn, gelatin, a small quantity of wax, and volatile oil; yellow silk also contains colouring matter (Roard). Mulder thought that he had found albumin, to the amount of 24 to 25 p. c., a statement which was called in question by Stadeler and refuted by Cramer. When fresh silk-cocoons are cut up, the still living larvæ removed, and the remaining substance digested with water at 40°—50°, a liquid is obtained containing silk-gelatin, but no albumin, inasmuch as it does not coagulate on boiling, even after addition of acetic acid, and is not precipitated by ferrocyanide of potassium (Cramer).

The juice contained in the sacs of the silk-worm, which is exuded by the animal in spinning, and hardens in contact with the air, is, according to Bolley, soft fibrin, which as it is spun, is converted on the surface into silk-gelatin. If the sacs preserved in alcoholic acetic acid be deprived of their easily separable skin, and the hard elastic contents be boiled for twelve hours with acetic acid, 8·14 p. c. is dissolved, and by boiling with water for 20 hours, 1·71 p. c. The undissolved residue exhibits the properties of fibroïn (Bolley, Züricher, *Mittheil.; J. pr. Chem.* 93, 347).

Fresh silk-substance is amber- to gold-yellow, transparent, tough; dissolves in water to a neutral gold-yellow liquid which froths up, but does not coagulate on boiling; solidifies to a tremulous jelly on standing, and does not become quite clear again when boiled. The solution is ropy while hot, and on addition of a drop of acid, deposits a flocculent coagulum which does not dissolve in a larger quantity of acid; if mixed at once with a considerable quantity of acid, it remains clear, but solidifies to a jelly after some hours. The solution assumes a dirty violet colour when boiled with strong hydrochloric acid, is not altered by soda-ley, and after boiling therewith, does not give off sulphuretted hydrogen on addition of hydrochloric acid; it is not precipitated by mercuric chloride, nitrate of silver, or ferrocyanide of potassium; acetate of lead and cupric sulphate produce a jelly; tannic acid throws down tenacious flocks (Ludwig, *N. Br. Arch.* 54, 142; *Ann. Pharm.* 68, 366; *Jahresb.* 1847—48, 936).

The constituents of the silk of the Chinese oak-spinner, the Jama-may silk of commerce, are the same as those of the silk of *Bombyx mori* (Bolley).

The cocoon of indigenous Bombyx caterpillars exhibits the same characters as silk (Schlossberger). Gossamer threads contain 15·25 p. c. fibroïn, also albumin (see above), jelly, cerin and solid fat (Mulder, *Pogg. Ann.* 39, 408). Spider-threads react like fibroïn (Schlossberger, *Ann. Pharm.* 110, 245).

Preparation. 1. Raw silk is boiled with strong acetic acid, and the undissolved portion is washed till it no longer exhibits an acid reaction (Mulder). — 2. Yellow raw silk is boiled in a Papin's digester for two or three hours six times in succession with water at 133°; the extracts containing the silk-gelatin are removed; and the residue is freed from colouring matter by treatment with strong alcohol, and from small quantities of fat by ether. Silk thus treated yields 66 p. c. fibroïn (Cramer). — 3. Yellow raw silk is immersed in cold soda-ley of 5 p. c.; the solution is expressed after 18 hours; the silk, which has become colourless, is washed first with pure water, then with water containing hydrochloric acid (1 pt. of fuming acid to 20 pts. water), and finally again with pure water; and the residue, amounting to 42—50 p. c. is dried (Städeler).

Properties. Colourless. Resembles cleansed silk, even when viewed under the microscope, but is easily torn, and according to Städeler, easily rubbed to a soft powder. Heavier than water.

					Städeler.	Cramer.		Vogel,
						a.	b.	jun.
30 C	180	48·77	47·83		48·60	48·39	48·06	49·99
5 N	70	18·97	17·36		18·89	18·40	18·21	19·03
23 H	23	6·24	6·54		6·40	6·51	6·02	6·88
12 O	96	26·02	28·27		26·11	26·70	27·71	24·10
$C^{30}N^5H^{23}O^{12}$	369	100·00	100·00		100·00	100·00	100·00	100·00

	Bolley.	
	a.	b.
30 C	47·08	48·50
5 N	17·70	18·89
23 H	7·20	6·58
12 O	28·02	26·03
$C^{30}N^5H^{23}O^{12}$	100·00	100·00

So according to Cramer; according to Mulder $C^{78}N^{12}H^{63}O^{32}$; according to Vogel, $C^{48}N^8H^{38}O^{17}$. — It still contained at most about 0·3 p. c. ash and traces of sulphur. Bolley's fibroïn *a* was taken from the vessels of the caterpillar and purified by boiling with water; *b* from Jama-may silk. Croockewit's analysis: *Ann. Pharm.* 48, 49.

Decompositions. 1. Yields by *dry distillation* a large quantity of ammonia carbonate, empyreumatic oil and water, and leaves a bulky charcoal. Softens when heated, burns away with an odour of horn and a light blue flame, and leaves a large quantity of charcoal. — 2. Dissolves only in small quantity when heated with *water* to 133°, and even to 170°, in large quantity if it has been previously exposed to the air; from the solution alcohol throws down a white precipitate, which does not form a jelly with water (Cramer). — 3. Dissolves in *nitric acid* all but a few flocks, and forms oxalic acid when heated (Mulder). From the nitric acid solution, ammonia throws down a yellow body having the composition $C^{48}N^6H^{38}O^9$ (A. Vogel). — 4. Warm *phosphoric acid* dissolves fibroïn with brown colour; cold strong *hydrochloric acid* dissolves it quickly, forming a colourless liquid which assumes a brown colour when heated (Mulder), a fine violet (Cramer). — 5. It dissolves in cold *oil of vitriol* to a thick light brown liquid which, when heated turns red, carbonises, and gives off sulphurous acid. From the sulphuric acid solution, which is miscible with water without precipitation, potash-ley throws down flocks soluble in excess of potash, and infusion of galls forms a copious white precipitate. — When fibroïn is boiled with a mixture of 1 vol. oil of vitriol and 4 vol. water, it dissolves easily, and forms (in 8 to 10 hours) tyrosine, amounting to 5—8 p. c. of the fibroïn (Städeler), and leucine (Hinterberger & Waltenberger, *Wien. Acad. Ber.* 11, 450); also traces of ammonia, sugar recognisable by an alkaline solution of cupric oxide, and, especially on long boiling, glycine (Städeler; Cramer). — 6. Heated for some time with strong *acetic acid*, it gives up to the acid about 6 p. c. of its weight, and on evaporation there remains a brown amorphous extract, only partly soluble in water; the portion insoluble in acetic acid exhibits the composition of unaltered fibroïn (Cramer). Pulverised fibroïn dissolves completely when boiled for several hours (Städeler); unpulverised fibroïn dissolves at 170° (Cramer). From the acetic acid solution, ammonia throws down a small quantity of a bulky precipitate.

The substance which passes into solution when silk, previously exhausted with water, alcohol, and ether, is boiled with strong acetic acid, is Mulder's *silk albumin*, which, moreover, remains undissolved when silk is boiled with water and alcohol, the liquid evaporated, and the residue exhausted with boiling water and alcohol. It is friable, heavier than water, burns with flame, and a smell of horn, leaving 11 p. c. ash, after deduction of which it contains 53·01 p. c. C., 15·23 N., 7·27 H., and 24·49 O. It dissolves in warm hydrochloric acid, also in acetic acid, forming a liquid which gives a green precipitate with ferrocyanide of potassium; also in aqueous ammonia, potash, and soda, and is precipitated therefrom by acids (Mulder).

7. Fibroïn heated with lumps of *potash-hydrate* forms oxalic acid (Mulder).

Combinations. Fibroïn, over which dry *hydrochloric acid gas* and afterwards air is passed, at 14°, increases in weight by 7·46 p. c., but easily gives up the hydrochloric acid again (Mulder). — Fibroïn does not dissolve in aqueous ammonia, or in dilute potash or carbonate of potash; the solution obtained with cold concentrated or dilute boiling potash-ley is precipitated by water and by acids, the fibroïn then separating in threads (Mulder), in bulky flocks (Cramer).

Silk dissolves quickly in warm aqueous *chloride of zinc*, slowly in the cold dilute solution, forming a glutinous syrup, from which water throws down a precipitate soluble in excess of ammonia. The solution diluted with aqueous hydrochloric acid loses in Graham's dialyser the whole of its zinc chloride, and leaves a clear tasteless solution, which dries up to a golden-yellow varnish. The concentrated solution changes in the dialyser into an insipid paste, not free from zinc, which dries up to a brittle glass, reddens when heated, and decomposes with the odour of burnt silk. It swells up with potash-ley, is not liquefied by sulphuric acid, dissolves in acetic acid while moist, but not after drying (J. Persoz, *Compt. rend.* 55, 810; *Chem. Centr.* 1863, 165).

Stannic chloride does not colour silk (Maumené, *Compt. rend.* 30, 447; *Jahresb.* 1850, 601).

In aqueous *niccolate of ammonia* (Schlossberger) and in aqueous *cuprate of ammonia* (Schweizer), both raw silk, and silk which has been well cleansed by boiling, swell up quickly and strongly, and soon dissolve. The nickel-solution is yellow-brown, the copper-solution bluish-violet; neither of these solutions is precipitated by alkaline salts, sugar, or gum; acids throw down colourless flocks which dissolve in excess of the acid; sal-ammoniac colours the nickel-solution bluish-violet. Solutions of the two oxides in carbonate of ammonia do not dissolve silk (Schlossberger, *Ann. Pharm.* 107, 26; 108, 62); see also Ozanam (*Compt. rend.* 55, 883).

Silk wetted with solution of *cupric nitrate*, and then with soda-ley, acquires a violet colour, and dissolves, together with cupric oxide, forming a blue, or with excess of silk, a violet, crimson, or blood-red solution (Vogel & Reischauer, *N. Repert.* 8, 529; *Chem. Centr.* 1860, 301; *Jahresber.* 1860, 566).

Silk immersed in solution of *picric acid* acquires a pure yellow colour (Pohl, *Wien. Acad. Ber.* 9, 386; *Jahresber.* 1852, 825). — Fibroïn is insoluble in *alcohol* and in *ether*.

Appendix to Fibroïn.

Silk-gelatin.

Mulder's *Silk jelly*. *Seidengallerte.*

Raw silk is boiled with water for three hours; the expressed liquid is precipitated with basic lead acetate; the washed precipitate decomposed under hot water with sulphuretted hydrogen; and the concentrated filtrate is mixed with a little alcohol, whereby a certain portion of the gelatin, together with suspended lead sulphide and the greater part of the salts, is precipitated. From the colourless filtrate the gelatin is thrown down by a larger quantity of alcohol, and purified by boiling with alcohol and ether (Cramer). Mulder's silk-jelly is obtained by boiling the silk with water, evaporating, exhausting the residue with alcohol and ether, dissolving in warm water, filtering, and evaporating. Bolley leaves Jama-may silk immersed for 24 hours in cold hydrochloric acid; washes away the acid, and with it the mineral constituents; boils for a long time with water; concentrates; mixes the cooled filtrate with a little alcohol; boils; and filters hot. By adding more alcohol to the filtrate, the silk-gelatin is precipitated in flocks.

White, scentless, and tasteless powder, or transparent gelatinous mass.

at 125° *to* 130°.			Cramer. *mean.*	Bolley.
30 C	180	44·67	44·32	44·22
5 N	70	17·62	18·30	18·64
25 H	25	6·21	6·18	5·81
16 O	128	31·50	31·20	31·33
$C^{30}N^5H^{25}O^{16}$	403	100·00	100·00	100·00

After deduction of 1·25 p. c. ash, it still contained traces of sulphur. — Mulder's analysis, made with substance containing 2 to 5·2 ash, yielded 41·6 to 48·5 p. c. C., 16·1 and 18 9 N.

Silk-gelatin, when *heated*, softens, swells up, emits an odour of burning horn, and leaves charcoal together with ash (Cramer). The solutions in *oil of vitriol* and in *phosphoric acid* carbonize when heated; that in *nitric acid* gives off nitrous gas, and forms oxalic acid (Mulder). When silk-gelatin is continuously boiled with dilute *sulphuric acid*, tyrosine (amounting to 5 p. c. of the gelatin) leucine, and serine are formed (Cramer).

Mulder thought that he had obtained sugar, but appears to have mistaken the sweet-tasting serine for that substance.

From the aqueous solution of silk-gelatin, *chlorine-water* throws down flocks which redden on exposure to the air, and dissolve in alcohol (Roard) *Iodine* does not alter the solution (Mulder).

Swells up when *water* is poured upon it, and dissolves in hot water more easily than common gelatin. Solutions containing 6 p. c. coagulate on cooling to a solid jelly, which is liquefied again by acetic acid, potash, or soda.

The aqueous solution is not altered by dilute *acids*, or by aqueous *alkalis*; it is precipitated by many *metallic salts*, especially by alum, aluminic, ferrous, ferric, and plumbic sulphates, neutral lead acetate (contrary to Mulder's statement), mercurous nitrate, silver nitrate, or platinic chloride, most of these precipitates dissolving in excess of the reagent, or when heated (Cramer). The solution mixed with acetic acid is not precipitated by *ferrocyanide* or *ferrocyanide of potassium* (Cramer); according to Mulder it forms with the ferrocyanide a precipitate of a fine green colour, soluble in water. — *Infusion of galls* and *tannic acid* throw down from the aqueous solution an abundance of white flocks.

Silk-gelatin is insoluble in boiling alcohol of sp. gr. 0·829 (Roard). Its aqueous solution is precipitated by *alcohol* and *ether* (Cramer). It does not dissolve in *volatile* or in *fixed oils* (Mulder).

The *colouring matter of yellow raw silk* is red-brown, or in powder greenish-yellow, resinous; it melts at 30°, emitting a strong odour arising from the volatile oil which it contains. It is converted by chlorine into a solid white wax, blackened by oil of vitriol and strong hydrochloric acid, and only slightly decolorised by sulphurous acid. Its concentrated solutions are bleached in a few days by exposure to light. — It is insoluble in water, slightly soluble in cold, somewhat more freely in hot aqueous ammonia, potash, and soda, more abundantly in hot soap-water; soluble in 8 to 10 pts. of alcohol (Roard).

Mulder (*Pogg.* 37, 610) exhausts silk successively with boiling water and boiling absolute alcohol, evaporates the liquid, and cools it repeatedly, whereupon cerin separates in flocks. The mother-liquor is evaporated to dryness and treated with strong potash-ley, whereby fat and resin are dissolved, while the colouring matter remains as a mass of a fine red colour, soluble in alcohol, ether, volatile oils, and fixed oils.

Yellow raw silk is bleached, with decomposition of the colouring matter, when exposed to sunshine for several hours or days in a mixture of sulphurous acid gas and air or oxygen; in the dark the colour disappears very slowly (Schönbein, *J. pr. Chem.* 89, 321).

The colouring matter of Jama-may silk dissolves in boiling alcohol containing hydrochloric acid, with green colour, and separates in green drops when the solution is concentrated, after precipitation with ammonia and oxalic acid. These drops dissolve with blue-green colour in ether, leaving a yellow residue, more of which may be obtained by repeatedly evaporating the ethereal solution (Bolley).

Serine.

$$C^6NH^7O^6 = C^6AdH^5O^6.$$

CRAMER. See memoir cited under Fibroïn (p. 363).

Amidoxypropionic acid, $C^4H^3(NH^2,O^2H),C^2O^2,O^2H$.

Formation. Together with leucine and tyrosine, by boiling silk-gelatin with sulphuric acid.

Preparation. Raw silk enclosed in a bag is evaporated till it softens, and then boiled for a short time with water; to obtain strong solutions, the boiling is several times repeated with fresh quantities of water, or the solution is concentrated. It is then boiled with ¼ vol. oil of vitriol, for 9 to 24 hours, the water being renewed as it evaporates, and the solution is supersaturated with lime, filtered, exactly neutralised with dilute sulphuric acid, and evaporated. Tyrosine and gypsum then separate out, afterwards druses of serine, and finally leucine. The serine is dissolved in cold water, and filtered from undissolved tyrosine; the gypsum is removed by treatment with baryta-water and carbonate of ammonia; the liquid left to crystallise; and the crystals, which are mostly reddish, are decolorised by dropping a small quantity of basic lead acetate into the solution, and treating the filtrate with hydrosulphuric acid.

Colourless, oblique rhombic crystals, frequently united in druses or in crusts. Neutral. Has a faint sweet taste.

	Crystals.		Cramer.
6 C	36	34·28	34·12
N	14	13·33	13·35
7 H	7	6·66	6·68
6 O	48	45·73	45·85
$C^6NH^7O^6$	105	100·00	100·00

Decompositions. Turns brown when heated, giving off an odour of burning horn. — *Nitrous acid* converts it into glyceric acid, with evolution of nitrogen:

$$C^6NH^7O^6 + NO^3,HO = C^6H^6O^8 + 2N + 2HO.$$

Dissolves in 24·2 pts. *water* at 20°. More easily in hot water. Unites with *bases* and with *acids*, but does not neutralise the latter. *Sulphate of serine* is crystalline.

Hydrochlorate of Serine, $C^6NH^7O^6,HCl$. Colourless, shining concentrically grouped needles. Easily soluble in water, sparingly in alcohol. Gives off hydrochloric acid when evaporated.

Nitrate of Serine. — Microscopic, very soluble needles, having the composition $C^6NH^7O^6,HO,NO^5$.

Aqueous serine dissolves carbonate of baryta on boiling, with evolution of carbonic acid, forming an alkaline liquid.

Serine with Cupric Oxide. — By boiling serine with cupric oxide, a deep blue solution is obtained, from which blue microscopic needles separate. They do not lose weight over oil of vitriol.

6 C	36	26·52	26·38
N	14	10·31	9·82
6 H	6	4·42	4·45
5 O	40	29·50	30·62
CuO	39·7	29·25	28·73
$C^6NH^6CuO^6$	135·7	100·00	100·00

Serine unites with *silver oxide.* — Its hydrochlorate does not combine with *platinic chloride.*

Serine is insoluble in *alcohol* and in *ether*.

Spongin.

POSSELT. *Ann. Pharm.* 45, 192.
CROOCKEWIT. *Ann. Pharm.* 48, 43.
SCHLOSSBERGER. *Ann. Pharm.* 108, 64; *Chem. Centr.* 1859, 77.
STÄDELER. *Ann. Pharm.* 111, 16; *Chem. Centr.* 1859, 705; *Jahresb.* 1859, 598.

The organic matter of sponges. — The tissue of sponge consists of a network of round, apparently solid fibres, $\frac{1}{40}$ mm. thick—Städeler's *spongin*—coated on the younger parts with a soft, flocculent, felted substance, forming the connecting material, and less abundant on the older parts of the tissue. This binding material is not altered by water containing hydrochloric acid, but is quickly dissolved by soda-ley of 5 p. c., whereas the threads remain undissolved for 24 hours (Städeler).

Sponge may be cleansed from sand by beating, cutting, pulverising, and sifting, and further purified by boiling with water containing hydrochloric acid, and with pure water (with ether and alcohol according to Posselt), but even then it yields 3·59 p. c. ash (Posselt), 3·7 p. c. (Croockewit).

Analyses of Sponge.

	Posselt. *mean.*	Croockewit. *mean.*
C	48·42	46·46
N	16·15	16·15
H	6·29	6·31
O	29·14	
	100·00	

Croockewit found also 1·09 p. c. iodine, which, however, might have been derived from the potash, (Städeler), 0·50 S., 1·90 P. He gives the formula $C^{30}N^{6}H^{3},O^{7}$, and regards spongin as identical with fibroïn, but combined with phosphorus, sulphur, and iodine. Schlossberger, also, who pointed out the difference between spongin and fibroïn, found in thoroughly washed sponge, phosphorus, sulphur iodine, and small quantities of chlorine and bromine.

Sponge loses its elasticity at 200°, without becoming friable or suffering further alteration. When further *heated* it decomposes without softening, exhaling an offensive odour, giving off carbonate of ammonia together with a small quantity of water, and leaving charcoal, together with a quantity of ash amounting, on the average, to 3·5 p. c. (Posselt). It is not altered by several hours' boiling with water, and does not yield gelatin when thus treated (Posselt; Städeler). — When boiled with *nitric acid* of sp. gr. 1·3, it forms a colourless solution (Städeler). Moderately dilute nitric acid dissolves part of it, and leaves the rest as a yellow, soft, slippery mass, insoluble in boiling water, dissolving with strong intumescence in ammoniacal water, easily, and with fine red colour in potash (Posselt). — Dissolves in oil of vitriol when heated, forming a solution which has a faint brown colour (Städeler), is not precipitated by water (ammonia, Posselt) or potash, but gives a precipitate with infusion of galls (Croockewit). If the dark-coloured oil of vitriol be poured off before the solution is complete, the residue, after washing with water, is brittle, but not soluble in boiling water (Posselt). —When comminuted sponge previously exhausted with dilute hydrochloric acid and with soda-ley of 5 p. c., is boiled with a mixture of 1 vol. oil of vitriol and 4 vol. water, it dissolves, and after ten hours' boiling, forms leucine and glycine, but not a trace of tyrosine (Städeler). — Strong *hydrochloric acid* dissolves the sponge slowly but almost completely, without colouring it blue; the solution (colourless even when boiled, Städeler) is not precipitated by ammonia, ferrocyanide of potassium, or mercuric chloride (Posselt). — Cold dilute mineral acids and strong *acetic acid* produce no alteration.

Sponge is not altered by aqueous ammonia. Dissolves very slowly or not at all in cold dilute *soda-ley;* easily at the boiling heat (Städeler). In rather strong *potash-ley* it dissolves in the cold, and more easily when warm, with yellow colour, and evolution of ammonia, which continues on prolonged boiling, even after complete dissolution, the liquid at the same time becoming red, thick, and tenacious; it is scarcely precipitable by acids, but gives off hydrosulphuric and carbonic acids when treated therewith (Posselt). In the alkaline solution, acids sometimes form a precipitate, and cupric acetate a second precipitate in the filtrate; on again filtering the solution, treating it with hydrosulphuric acid, and neutralising with potash-ley, it still gives a precipitate with neutral lead acetate on addition of ammonia (Croockewit).

Baryta-water dissolves sponge at the boiling heat, with transient red, and afterwards yellow colour, and on treating this solution with carbonic acid, removing the carbonate of baryta which contains a small quantity of organic substance, precipitating (*a*) with neutral acetate of lead, decomposing the precipitate with hydrosulphuric acid, and filtering, the filtrate leaves on evaporation a brown residue, the aqueous solution of which is precipitated by tincture of galls, but not by mercuric chloride or ferrocyanide of potassium. This residue is insoluble in alcohol. — *b*. When the liquid which runs off from the lead precipitate is freed by sulphuric acid from lime and baryta, it leaves on evaporation a brown deliquescent mass, to be further separated by alcohol. — *c*. The portion insoluble in alcohol yields, when digested with litharge, a lead-compound, which, after evaporation, no longer dissolves completely in water; it contains 17·50 p. c. lead oxide, after deduction of which it yields on the average, 45·8 p. c. C., 14·8 N., 6·3 H., and 33·1 O. — *d*. The portion soluble in alcohol also yields a soluble lead-salt containing 17·04 p. c. PbO., while its organic substance contains 46·2 p. c. C., 5·8 N., 6·3 H., and 41·7 O. Its solution is precipitated by tincture of galls, not by ferrocyanide of potassium or acetate of lead (Posselt).

Chlorine gas passed through the dark brown solution of sponge, obtained by digestion with potash and neutralised with hydrochloric acid, decolorises it, and separates a viscid scum, which settles down in the form of a white curdy mass; this substance contains chlorine, and has a golden-yellow colour when dry (Croockewit). — When sponge, after treatment with hydrochloric acid, but not with soda-ley, is immersed for 20 to 30 hours in aqueous *cuprate of ammonia*, it shrinks very much, and becomes easily friable, even the fibres being strongly attacked (Städeler; Schlossberger, *Krit. Zeitschr.*, 1860, 426). With soda-ley and cupric sulphate the substance of sponges behaves like fibroïn (Vogel & Reischauer). On its behaviour to red colouring matters, see Böttger (*J. pr. Chem.* 91, 246).

Conchiolin.

FRÉMY. *Compt. rend.* 39, 1052; *N. J. Pharm.* 27, 5; *J. pr. Chem.* 64, 257; *Pharm. Centr.* 1855, 68 and 129; in full: *N. Ann. Chim. Phys.* 43, 96; *Jahresb.* 1854, 710.

SCHLOSSBERGER. *Ann. Pharm.* 98, 99; *Chem. Centr.* 1856, 487; *J. pr. Chem.* 68, 162; *Jahresb.* 1856, 714. — *Krit. Zeitschr.* 1860, 424; *Jahresb.* 1860, 570.

Occurrence. In certain mussel-shells. In the horny axis of Gorgonia there occurs a similar substance, containing 49·4 p. c. C., 16·8 N., 6·3 H., and 27·5 O. (Fremy). Compare xv. 414.

Remains when mussel-shells are treated with hydrochloric acid, as a shining felted residue, which is insoluble in water, alcohol, and ether, does not yield gelatin when boiled with water, and is but very slowly dissolved by concentrated acids or alkalis. It contains 50·0 p. c. C., 17·5 N., 5·9 H., and 26·6 O.; when treated with hydrochloric acid, in contact with the air, it does not exhibit a blue colour like the albuminates (Frémy).

The residue left on treating oyster-shells with very dilute hydrochloric acid may be resolved, by levigation with a large quantity of water, into two substances, one of which consists of thick brown membranes, the other of white or grey flocks. These two substances belong to different layers of the shell, the flocks to the innermost, or mother-of-pearl layer, and to the chalk-layer interposed between the lamellæ of the shell; the membranes to the brown hard scales of the shell (Schlossberger).

The *brown membranes*, after washing and drying, are greyish-yellow, nearly opaque, and exhibit, when examined by the microscope, a brown amorphous ground-substance with numerous colourless spots, mostly of regular rhombic form. These membranes do not dissolve in over-heated water, boiling acetic acid, alcohol, or ether. In cold oil of vitriol they swell up, become soft and transparent, dissolve with yellow colour when heated, and afterwards carbonise. The only crystallisable product obtained by boiling them with dilute sulphuric acid is leucine.—Nitric acid colours the membranes pure yellow when heated with them, and dissolves them with brown colour at the boiling heat.—Strong potash-ley, boiled with the membranes or left in contact with them for a week, colours them yellow-brown, and dissolves about 46 p. c. of them, leaving the remainder externally unaltered; the residue and solution exhibit the following characters.—*a.* The *residue* is a powder of a somewhat paler brown than the original membranes, greyish-yellow after drying, containing 50·7 p. c. C., 16 to 16·7 N., 6·5 H., no sulphur, but still 1 p. c. of mineral substances. When heated, it carbonises, emitting an odour of horn, but does not melt. When fused with potash-hydrate, it gives off ammonia, assumes a transient rust-yellow colour, and then dissolves in acids, forming a yellow liquid.—*b.* The alkaline solution is not precipitated by acids, and only slightly by ferrocyanide of potassium after supersaturation with acetic acid; the residue, saturated with carbonic acid and evaporated, yields to alcohol a yellow nitrogenous substance.

The *white flocks* are obtained in small quantity only. They dissolve with brown colour in strong boiling potash-ley, are not precipitated by acids, and react in general like the portion of the brown membranes which is soluble in potash (Schlossberger).

Byssus of the Acephalæ.—According to Leuckart (*Wiegmann's Arch.* 1852, 25) it contains chitin (xv, 414). When the byssus of *Pinna nobilis* is repeatedly boiled with potash-ley of 20 p. c. as long as the liquid becomes coloured, there remain brown, swollen, gummy threads, which, when washed, recover the original appearance of the byssus, and appear rotten and brittle after drying. The substance thus purified exhibits the following reactions: it is not altered by dilute acids; is slowly coloured yellow by strong nitric acids; then dissolved to a yellow liquid, from which, after neutralisation with ammonia, tannic acid and basic acetate of lead throw down precipitates. By boiling with hydrochloric acid, the root-parts become fragile; the ends of the threads reddish brown, with an almost coppery lustre after drying; after boiling for ten minutes the threads are incompletely dissolved, and a brown solution is formed. Oil of vitriol does not alter the substance at first, but afterwards colours it bright-red, without dissolving it, even after several weeks' contact.—Alkaline water restores the brown colour. Hot oil of vitriol dissolves it, forming a black-brown liquid which yields a copious precipitate with tannic acid after neutralisation. Dilute sulphuric acid at 120° partly dissolves the substance and carbonises the rest. Tincture of iodine does not alter it; addition of oil of vitriol produces red-brown coloration. This substance chars when heated, without melting, like chitin, and contains 13·5 to 13·9 p. c. nitrogen (12·2 to 12·6 p. c. when the byssus was treated with boiling potash-ley, then with acetic acid and water), and is, therefore, different both from chitin and from conchiolin. It is completely decomposed by fusion with potash-hydrate, assuming at the same time a bright rust-yellow colour (Schlossberger, *Ann. Pharm.* 98, 109).

Hyalin.

A. Lücke. *Verch. Arch.* 19, 189.

Discovered by Lücke, named by Hoppe-Seyler. Forms the coarse, elastic, structureless membranes of the mother-bladders of echinococci, which in the younger individuals are milk-white and opaque, in older or dead ones, gelatinous and transparent.

The membranes, purified by washing with water and alcohol, are friable when dry; the younger ones contain 15·8, the older 0·29 p. c. ash, which is not removed.

After deduction of the Ash.

	Young Bladders.	Old Bladders.
C	43·05 to 44·58	44·87 to 45 72
N	4·29 „ 4·65	5·11 „ 5·21
H	6·53 „ 6·90	6·40 „ 6·73

Hyalin from old bladders, heated with water to 150° in a Papin's digester, dissolves to a clear liquid, which when evaporated leaves a residue easily soluble in cold water. This solution is precipitable by neutral and basic acetate of lead, mercuric nitrate, and alcohol; not by chlorine-water, mercuric chloride, silver nitrate, potassium ferrocyanide, or tannic acid. Hyalin from young bladders yields at 150° a turbid solution and a ropy residue, and on evaporation there remains a residue sparingly soluble in boiling water.—Dilute *hydrochloric acid* colours hyalin violet after long standing; boiling concentrated hydrochloric acid and *nitric acid* dissolve it completely; dilute *sulphuric acid* partially. When hyalin covered with oil of vitriol is left to itself for a while and the mixture dropt into boiling water, or when hyalin is boiled for a long time with dilute sulphuric acid, dextroglucose is formed, together with a nitrogenous substance precipitable by alcohol in flocks. The quantity of sugar thus obtained from hyalin of young bladders appears to vary between 20·9 and 50 p. c.; that from the hyalin of old bladders, between 24·5 and 43 p. c.

Hyalin from old bladders dissolves but incompletely in *potash-ley* even after prolonged boiling; that of the young bladders colours the ley lemon- or greenish-yellow.

Insoluble in *water*, *alcohol*, and *acetic acid*.

Neorsin.—Occurs to the amount of 90·26 p.c. in the edible swallows' nests of Java, and contains 54·81—55·05 p. c. C., 7·06 H., 11·65 N. (Mulder, *Nat. en Scheikund. Archief.* 1838, 172; *Berzel. Jahresb.* 19, 720).

Lecithine.

LIEBREICH. *Ann. Pharm.* 134, 29; *Chem. Centr.* 1865, 666; *Jahresb.* 1865, 647.

HOPPE-SEYLER. *Tubinger medic. Unters.* 1, 140; abstr. *Analyt. Zeitschr.* 5, 422; *Jahresb.* 166, 744; *Tubinger medic. Unters.* 1, 215; *Chem. Centr.* 1868, 136; *Jahresb.* 1867, 774.

DIAKONOW. *Tübinger medic. Unters.* 1, 221; *Chem. Centr.* 1868, 138; *Medecin. Centr.* 1868, 97, 434; *Chem. Centr.* 1868, 140, 169, 515. — *Tubinger medic. Unters.* 1, 405.

STRECKER. *Zeitschr. f. Chem.* [2], 4, 437; *Chem. Centr.* 1868, 516; in full: *Ann. Pharm.* 148, 77.

After the occurrence of phosphoretted compounds in the animal body had been established (xvi, 483), Liebreich obtained, as a product of the decomposition of choline (p. 378), a mixture containing lecithine, which he denominated *Protagon*. From the results of experiments by Parke and Hoppe-Seyler, Diakonow concluded that protagon is a mixture of cerebrin (xvi, 479) and lecithine, which latter he obtained in the pure state and examined.

Occurrence. In yolk of egg (Gobley, xvi, 484; Diakonow), and either wholly or partially as vitellin, in combination with albumin (Hoppe-Seyler). In the brain; probably also generally diffused in the animal body and in plants (Liebreich).

On the occurrence of lecithine in the blood, see L. Hermann (*Muller's Arch.* 1866, 33; *Zeitschr. f. Chem.* [2], 2, 250); G. Jüdell (*Tubinger medic. Unters.* 1, 386); in milk (Tolmatscheff, *ibid.* 1, 272). Hoppe-Seyler found lecithine in the seminal fluid of animals, abundantly in the electric organs of the torpedo, in maize-seed, in yeast, in the eyes of roses, and in caviare; he supposes it to exist in all organs in which protagon (*infra*) or phosphoretted fats (xvi, 483) have been detected.

The phosphoretted bodies, *Myeloïdin*, *Myeloïdic acid*, *Neurolic acid*, prepared from brain by H. Köhler (*Virch. Arch.* 45, 265; *Chem. Centr.* 1867, 406 and 1022; *Jahresber.* 1867, 809) owe their phosphorus to an admixture of lecithine, which is easily precipitated simultaneously with other bodies (Diakonow).

Microscopic primitive forms which were obtained by Virchow (*Virch. Arch.* 6, 502) from nervous tissue after prolonged contact with water, frequently also observed in pathological formations, and designated as *Myelin-forms*, were afterwards regarded as characteristic of the occurrence of chemically definable substances. They consist of many-formed threads, globules, and drops of a viscid mass, which are likewise obtained from alcoholic extracts of diseased liver, spleen, and kidneys (Meckel), from brain-substance, pancreas, egg-yolk, and pus (Virchow), from the lens of the eye (Mettenheimer.) — Beneke (p. 100) regarded myelin as a mixture of cholesterin and gallate of glyceryl, and found this myelin to be generally diffused in animal and vegetable organisms, especially where the existence of cholesterin and protagon or lecithine was subsequently demonstrated. — Liebreich (*Analyt. Zeitsch.* 4, 173) obtained myelin-forms by bringing protagon into contact with neurine and other bases (ammonia, potash, or soda), or by mixing a non-phosphoretted body resulting from the decomposition of protagon by hydrochloric acid, with fatty acids and alkali; lastly, Neubauer (*Analyt. Zeitsch.* 6, 189) obtained these forms by mixing oleic acid with ammonia and water. The occurrence of myelin-forms is therefore not associated with any definite chemical basis, but must be ascribed simply to the physical constitution of the material (Neubauer; Kraut, *Liter. Centralbl.* 1863, 491).

Preparation of Lecithine. From *Brain.* Finely pulverised brain freed from blood and membranes is exhausted with ether; the residue is treated at 40° with absolute alcohol; and the extract is cooled to 0°. A mixture of lecithine and cerebrin then separates, which is to be washed with a small quantity of cold absolute alcohol and exhausted with ether, which leaves cerebrin and protagon, and dissolves lecithine. The ethereal solution is evaporated, and the residue is dried at 40°, dissolved in a small quantity of absolute alcohol, and cooled to between − 7° and − 10°, whereupon bistearyl-lecithine separates and bioleyl-lecithine remains dissolved (Diakonow).

When chloroplatinate or chlorocadmiate of lecithine is treated with hydrosulphuric acid, the precipitated metallic sulphide removed, the excess of hydrosulphuric acid expelled by carbonic acid, and the liquid evaporated, hydrochlorate of lecithine remains as a waxy mass, which, when its ether-alcoholic solution is agitated with silver oxide, the dissolved silver removed by hydrosulphuric acid, and the liquid evaporated, yields lecithine.

For the detection of *protagon*, Hoppe-Seyler avails himself of the occurrence of phosphoretted products in its decomposition. He exhausts the liquid under examination with ether; separates the ethereal extracts from the watery liquid by decantation and filtration; distils; and boils the residue with concentrated alcoholic potash. On evaporating the alcohol, dissolving the residue in water, and exhausting with ether, the ether takes up the cholesterin which is generally present; and on decomposing the soap with hydrochloric acid, and removing the resulting fatty acids by agitation with ether, an aqueous solution is left, containing glycerophosphoric acid, which may be recognised by evaporating, fusing the residue with nitre and carbonate of soda, and testing for phosphoric acid.

Properties. Lecithine is a yellowish-white, waxy, very hygroscopic, amorphous mass, having a silky lustre in thin layers (Diakonow).

	a.			*b.*	
88 C	528	65·43	88 C	528	65·75
N	14	1·73	N	14	1·74
90 H	90	11·16	86 H	86	10·71
P	31	3·84	P	31	3·86
18 O	144	17·84	18 O	144	17·94
$C^{88}NH^{90}PO^{18}$	807	100·00	$C^{88}NH^{86}PO^{18}$	803	100·00

80 C	480	63·91
N	14	1·87
82 H	82	10 92
P	31	4·13
18 O	144	19·17
$C^{80}NH^{82}PO^{18}$	751	100·00

	Diakonow.	Strecker.	Liebreich.
C	64·27	64·6	66·77
N	1·80		2·80
H	11·40	10·7	11·63
P	3·62		1·23
O	18·91		17·57
	100 00		100·00

Lecithine is free from sulphur (Diakonow).

Diakonow's formula contains 1 at. water more than *a*. On the ground of its decomposition-products, lecithine must be regarded as a conjugated compound of neurine (choline) glycero-phosphoric acid and one or more fatty acids; Diakonow assumes, indeed, the existence of a bistearyl-lecithine (*a*) and a bioleyl-lecithine (*b*). Strecker, who likewise regards as probable the existence of several lecithines containing the radicals of different fatty acids, regards the lecithine which he examined as an oleyl-palmityl-lecithine containing equal numbers of atoms of the radicals of oleic and palmitic acid. Its formula, $C^{84}NH^{84}PO^{18}$ requires 64·8 p. c. C., 10·8 H.; the formula *c* is that of a palmityl-lecithine.

The atomic formula of lecithine is, according to Diakonow ($R = \text{Ꞓ}^{18}H^{35}\Theta$ or a similar radical, $\text{Ꞓ} = 12$, $\Theta = 16$).

$$\left.\begin{array}{l}R\,.\,\Theta\\ R\,.\,\Theta\end{array}\right\}\text{Ꞓ}^3H^5\,.\,\Theta\,.\,P\Theta\,.\begin{array}{l}\Theta\,.\,H\\ \Theta\,.\,N\,.\,3(\text{Ꞓ}H^3)\,.\,\text{Ꞓ}H^2\,.\,\Theta\,.\,H.\end{array}$$

According to Strecker's more probable view, which is corroborated by the composition of the chloroplatinate, it is

$$\left.\begin{array}{l}R\,.\,\Theta\\ R\,.\,\Theta\end{array}\right\}\text{Ꞓ}^3H^5\,.\,\Theta\,.\,P\Theta\,.\begin{array}{l}\Theta\,.\,H\\ \Theta\,.\,\text{Ꞓ}H^2\,.\,\text{Ꞓ}H^2\,.\,3(\text{Ꞓ}H^3)\,.\,\Theta\,.\,H.\end{array}$$

According to the former view, lecithine is a salt; according to the latter, it is an ammonium-base.

For *protagon* Liebreich gave the formula $C^{232}N^4H^{241}PO^{44}$, which requires 1·50 p.c. phosphorus; but Parke (*Tübinger medic. Unters.* 1, 209; *Chem. Centr.* 1868, 134) showed that the alcoholic extract of egg-yolk exhausted with ether contains a quantity of phosphorus larger than that which corresponds with the formula of protagon, and thereby demonstrated the existence of a more highly phosphorised compound in egg-yolk. Diakonow succeeded in resolving protagon, by means of ether, into a residue containing less, and a solution containing more phosphorus—ultimately, in fact, into lecithine and cerebrin. To the presence of this latter body is due the production of grape-sugar in the decomposition of protagon, as observed by Baeyer & Liebreich (*Virch. Arch.* 39, 183; *Chem. Centr.* 1867, 409).

Decompositions. 1. Lecithine becomes soft and transparent when *heated;* turns brown at 55°; gives off at 70° an odour of burning fat; and melts at 90°—100° to a black liquid, which when further heated burns with a bright smoky flame, leaving charcoal and ultimately phosphoric acid (Diakonow). — 2. The aqueous emulsion of lecithine, heated in a sealed tube to 120°, forms an upper oily layer containing fat and fatty acids, together with undecomposed lecithine, while the lower watery layer contains choline, phosphoric acid, and glycerophosphoric acid (Diakonow). — 3. Dilute *sulphuric acid* resolves lecithine into choline and *bistearyl-glycerophosphoric acid*, which forms a crystalline salt with potash (Diakonow). — 4. Lecithine heated with *baryta-water* is decomposed, with separation of stearate (palmitate, oleate) of baryta, and formation of glycero-phosphate of baryta and choline.

Formula for the decomposition, supposing stearic acid to be produced:

$$\begin{array}{ccccccccc} C^{88}NH^{90}PO^{18} & + & 6HO & = & 2C^{36}H^{36}O^{4} & + & C^{6}H^{9}PO^{12} & + & C^{10}NH^{15}O^{4}. \\ \text{Lecithine.} & & & & \text{Stearic acid.} & & \text{Glycerophosphoric acid.} & & \text{Choline.} \end{array}$$

a. The base formed in this reaction is *choline*, Liebriech's bilineurine, $C^{10}H^{15}NO^{4}$ = hydrated oxide of trimethyl-oxethyl-ammonium (p. 378), (Diakonow; Strecker). Pure protagon yields, not this base, but hydrated oxide of trimethyl-vinyl-ammonium, $C^{10}NH^{13}O^{4}$, whose gold-salt is easily recrystallised, and whose recently precipitated platinum-salt, if immediately dissolved and recrystallised, separates in yellow, distorted, five-sided tables. On recrystallising these tables, a salt, insoluble in water, remains behind, while the oxethyl-ammonium salt passes into solution. Lecithine from egg-yolk, bile, or the mother-liquors of protagon containing decomposition-products, yields only the oxethyl base (Liebreich, *Deutsche chem. Gesellsch.* 2, 12). See also Baeyer (*Ann. Pharm.* 140, 306; 142, 322), and Wurtz (*Deutsche chem. Gesellsch.* 2, 125), who appear to regard the base prepared from brain as a mixture of the oxethylated and vinylated bases.

b. The fatty acids produced in the above reaction are palmitic and oleic acid (Strecker); stearic or oleic acid, according to the way in which the lecithine has been prepared, the less soluble lecithine yielding only stearic, and no oleic acid, or only a trace of it, whereas the more soluble lecithine yields oleic with only a small quantity of stearic acid. When protagon instead of lecithine is used, the baryta-salt which separates is mixed with cerebrin (Diakonow).

Combinations. Lecithine swells up in *water*, forming a paste which is difficult to filter; with a larger quantity of water it forms an emulsion (Diakonow). In does not dissolve in dilute *acids* (Diakonow).

Hydrochlorate of Lecithine. — May be obtained from the chloroplatinate. — Waxy mass, from whose alcoholic solution oily drops of a fatty acid separate after long standing (Strecker).

Chlorocadmiate of Lecithine. — An alcoholic solution of cadmium chloride, added to an ether-alcoholic solution of lecithine, throws down white flocks, which may be washed with ether-alcohol without much loss by solution. — Soluble in alcohol containing hydrochloric acid (Strecker). After drying in a vacuum, it contains a quantity of cadmium, as chloride, varying between 13 and 15·2 p. c.; the organic substance exhibits the composition of lecithine (Strecker).

Chloroplatinate of Lecithine. — Lecithine is prepared by exhausting egg-yolk with ether-alcohol; the ether is distilled off; the fatty oil precipitated by mixing the residue with alcohol; and the remaining liquid is mixed with an alcoholic solution of platinic chloride. The copious yellow flocks thereby separated are purified by dissolving them five or six times in ether and precipitating with alcohol; they easily cohere when shaken, and may be dried in a vacuum without becoming insoluble in ether. — The salt melts at 100°, turning black and losing weight at the same time. It dissolves easily and abundantly in sulphide of carbon, ether, chloroform, and benzene; the ethereal solution, on standing, deposits chloroplatinate of choline (Strecker). A similar decomposition was observed by Hoppe-Seyler (*Tubinger medic. Unters.* 1, 411), who found that lecithine was but incompletely precipitated by platinic chloride.

	In vacuo.		Strecker.	
84 C	504	52·22	51·93	52·2
N	14	1·45		
83 H	83	8·59	8·63	8·9
P	31	3·21	3·55	3·2
Pt	98·7	10·23	9·23	9·9
3 Cl	106·5	11·03	9·50	
16 O	128	13·27		
$C^{84}NH^{82}PO^{16}$,HCl,$PtCl^{2}$	965·2	100·00		

Lecithine is insoluble in aqueous alkalis (Diakonow), but unites, according to Strecker, with bases. It dissolves *silver oxide.* From its ether-alcoholic solution, alcoholic *potash* throws down a crystalline precipitate, probably of lecithine-potash (Strecker).

Insoluble in aqueous *chloride of sodium;* easily soluble in *ether*, easily in hot *alcohol*, less easily in cold alcohol (Diakonow).

Appendix to Lecithine.

Choline or Neurine.

$C^{10}HN^{13}O^{2}$.

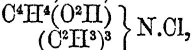
STRECKER. *Ann. Pharm.* 123, 353; *Krit. Zeitschr.* 1862, 558; *Répert. Chim. pure*, 5, 159; *Jahresber.* 1862, 540; Preliminary notice, *Compt. rend.* 52, 1270; *Jahresber.* 1861, 797; further, *Zeitschr. f. Chem.* [2], 4, 218, 439.

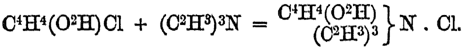
LIEBREICH. *Ann. Pharm.* 134, 29; *Par. Soc. Bull.* [2], 4, 400; *Jahresber.* 1865, 648.

BAEYER. *Ann. Pharm.* 140, 306; 142, 322.
DYBKOWSKY. *J. pr. Chem.* 100, 153; *Chem. Centr.* 1867, 225.
A. CLAUS & KEESÉ. *J. pr. Chem.* 102, 24.
AD. WURTZ. *Compt. rend.* 65, 1015.

Neurine.—Discovered in the bile of the pig and ox by Strecker, who called it *choline*, and by Liebreich, who called it *neurine.* Dybkowsky demonstrated the identity of the two bases thus named.—Wurtz discovered the synthesis of neurine.—Baeyer suspects that sincaline (xiv, 523) may also be identical with neurine, a supposition which appears to be corroborated by the preliminary investigation of Claus & Keesé.

Formation. 1. The hydrochlorate of this base, $C^{10}NH^{13}O^2,HCl$, or chloride of oxethyl-trimethyl-ammonium, $C^{10}NH^{14}O^2Cl = \left.\begin{matrix} C^4H^4(O^2H) \\ (C^2H^3)^3 \end{matrix}\right\} N.Cl$, is formed by heating ethyl-glycolic chlorhydrin (hydrochloride of ethylene-oxide; *Addenda*, xiii, 627) with trimethylamine (Wurtz):





$$C^4H^4(O^2H)Cl + (C^2H^3)^3N = \left.\begin{matrix} C^4H^4(O^2H) \\ (C^2H^3)^3 \end{matrix}\right\} N . Cl.$$

In like manner, amyl-glycolic chlorhydrin heated with excess of ammonia yields the chloride of hydroxamyl-ammonium, $C^{10}NH^{14}O^2Cl$, isomeric with hydrochlorate of choline: $C^{10}H^{10}(O^2H)Cl + H^3N = C^{10}H^{10}(O^2H),H^3N,Cl$; and ethyl-glycolic chlorhydrin heated with triethylamine yields the chloride of oxethyl-triethyl-ammonium, $C^{16}NH^{20}O^2Cl$, homologous with hydrochlorate of choline: $C^4H^4(O^2H)Cl + (C^4H^5)^3N = C^4H^4(O^2H),(C^4H^5)^3N,Cl$ (Wurtz).

2. Together with glycerophosphoric acid and fatty acids (Liebreich), by boiling protagon (from brain) with baryta. In this manner also choline is obtained from bile, in which only a very small quantity of it exists ready formed (Dybkowsky).—3. Lecithine (from egg-yolk) is resolved by boiling with baryta into stearic acid, glycerophosphoric acid and neurine (Diakonow). See page 377.

Preparation. 1. When 1 part of trimethylamine is heated with 2 pts. of glycolic chlorhydrin to 100° for 24 hours, the resulting solution yields on cooling, crystals of hydrochlorate of neurine, from which the base may be separated by moist oxide of silver (Wurtz).

3. Protagon is boiled for 24 hours with concentrated baryta-water; the excess of baryta is precipitated by carbonic acid, and the glycerophosphoric acid from the concentrated filtrate by basic acetate of lead; the filtrate is freed from lead by sulphuretted hydrogen, and evaporated to dryness with oxalic acid to remove acetic acid; the residue is digested with water and carbonate of baryta; the liquid filtered; and the chloroplatinate of neurine precipitated from the filtrate by hydrochloric acid and platinic chloride (Liebreich). Baeyer purifies crude hydrochlorate of neurine by precipitation with phosphotungstic acid; decomposes the washed precipitate with baryta-water; and evaporates the resulting liquid to a syrup, after removing the baryta with hydrochloric acid. There then remains colourless hydrochlorate of neurine, which is further purified by precipitating it as chloroplatinate with platinic chloride and alcohol, and separated therefrom by sulphuretted hydrogen.

Instead of protagon, fresh ox-brain freed from membranes and blood-coagulum may be used: it is triturated, stirred up with water, and exhausted with ether, or according to Claus & Keesé, with ether-alcohol (Dybkowsky). The ether-alcoholic extract is mixed with baryta-water, heated for 24 hours in the water-bath to decompose protagon and evaporate off the ether and alcohol, then concentrated to a syrup, exhausted with absolute alcohol, and precipitated with hydrochloric acid and platinic chloride. The yellow precipitate (which is increased in quantity by addition of ether, but does not then contain more neurine), is freed, by solution in boiling water and recrystallisation, from small quantities of chloroplatinate of ammonium and a compound easily soluble in cold water (Claus & Keesé; Dybkowsky).

Diakonow (*Chem. Centr.* 1868, 138) boils the ethereal extract of egg-yolk (or caviare) continuously with baryta; passes carbonic acid into the filtrate; acidulates; precipitates with phosphomolybdic acid; decomposes the precipitate with baryta; frees the filtrate from excess of baryta; acidulates; evaporates; exhausts the residue with alcohol; and precipitates the neurine with platinic chloride.

4. From *Pig-bile.* The bile is treated with hydrochloric acid to precipitate hyoglycocholic acid, mucus, &c.; the filtrate is evaporated, the residue exhausted with alcohol, which leaves common salt undissolved; the alcohol is evaporated; the residue again taken up with water; and alkalis, lime, and magnesia, are completely removed by evaporation with sulphuric acid, and further treatment the of residue with absolute alcohol. From the alcoholic solution thus obtained, ether precipitates a brown greasy mass, which is repeatedly treated with ether to remove lactic acid, dissolved in alcohol, mixed with water, and after the alcohol has been removed by boiling, further boiled with hydrated oxide of lead as long as ammonia continues to escape.

By removing the lead from the filtrate with sulphuretted hydrogen, evaporating to dryness, and redissolving the residue in absolute alcohol, a solution is obtained which deposits a tough glutinous mass, while choline remains in solution and may be precipitated as chloroplatinate by mixing the solution with hydrochloric acid and platinic chloride (Strecker).

Dybkowsky evaporates the bile to dryness; dissolves the residue in alcohol; precipitates with ether; stirs up the precipitate well with ether alcohol; distils; and boils the residue for 12 to 24 hours with baryta-water. The liquid, concentrated after removal of the excess of baryta with carbonic acid, is mixed with absolute alcohol; the precipitate is washed therewith, and the alkaline solution neutralised with hydrochloric acid, whereupon crystals of taurine separate; their deposition may be facilitated by leaving the liquid to itself for a day, and adding a little ether. From the filtrate, platinic chloride, after addition of more ether, if necessary, throws down yellow flocks, which are washed with ether-alcohol and dissolved in hot water; and the solution, after being freed by filtration from brownish adhesive flocks which separate on cooling, is again left to crystallise. There then appear orange-red tables and yellow octohedrons, the latter to be separated by trituration with water till the choline-salt is dissolved, then filtering, and evaporating the filtrate over oil of vitriol.

Aqueous neurine leaves on evaporation a strongly alkaline syrup, which contains a little silver, and decomposes when heated (Hoppe-

Seyler, *Handb. der physiol. u. pathol. Analyse*, 2 Aufl. 1865, 123.—Wurtz.) The decomposition of the aqueous solution by heat is attended with formation of trimethylamine, whence, as well as from the synthetic formation (p. 379), it follows that neurine has the constitution of hydrated oxide of *trimethyl-oxethyl-ammonium*, $N,(C^2H^3)^3,C^4H^4(O^2H),HO^2$, the chloride corresponding to which is $N,(C^2H^3)^3,C^4H^4(O^2H),Cl$. But when neurine is heated with excess of hydriodic acid, it gives up water, and yields the iodine-compound $C^{10}NH^{13}I^2 = C^{10}NH^{15}O^4 + 2HI - 4HO$, that is to say, *iodide of trimethyl-iodethyl-ammonium*, $(C^2H^3)^3,C^4H^4I,N.I$, which, in contact with silver oxide, yields no longer neurine, but the base $C^{10}NH^{13}O^2$, that is to say, *hydrated oxide of trimethyl-vinyl-ammonium*, $(C^2H^3)^3,C^4H^3,N.HO^2$ (Baeyer).

Combinations. The *carbonate* is amorphous, deliquescent, and has a strong alkaline reaction; its aqueous solution is not precipitated by alcohol. — The amorphous *sulphate* dissolves easily in dilute, with difficulty in absolute alcohol. — The *hydrochlorate* (= $C^{10}NH^{13}O^2,HCl$, Baeyer) forms deliquescent slender needles (Strecker, Liebreich). It dissolves very abundantly in boiling alcohol, crystallises from the highly concentrated solution in beautiful colourless prisms, and is precipitated by ether (in presence of traces of water, as an oil). Wurtz.

Chloroplatinate of Neurine. Crystallises from the mixed solutions in thin orange-yellow laminæ having the form of gypsum, and is precipitated from its aqueous solutions by alcohol (Strecker, Liebreich). Broad tabular prisms, terminated by rhombic pyramids with angles of 128° and 121°; the same angles are exhibited by the choline salt (Naumann). The hot-saturated solution deposits small needles, and on further evaporation over oil of vitriol, thick prisms; but when it is mixed with a slight excess of platinic chloride, rhombic prisms make their appearance, resembling the chloroplatinate of sincaline (xiv, 524) Claus & Keesé. — It is very apt to blacken during concentration, with formation of trimethylamine. — Does not give off any water at 110° (Dybkowsky).

			Strecker.	Liebreich.	Dybkowsky.
10 C	60	19·39	19·52	19·72	19·27
N	14	4·52	4·37	4·22	4·49
14 H	14	4·52	4·50	5·28	4·72
2 O	16	5·17		2·11	
Pt	99	31·99	31·75	33·27	31·92
3 Cl	106·5	34·41		35·40	
$C^{10}NH^{13}O^2,HCl,PtCl^2$	309·5	100·00		100·00	

Baeyer's analyses gave numbers varying from 19·54 to 20·74 p. c. for C., 4·58 to 5·0 for H., 30·87 to 32·74 for Pt.: hence he at first regarded neurine as a mixture of different bases. — This salt has also been analysed by Diakonow.

Chloroaurate of Neurine. — Auric chloride throws down from moderately diluted hydrochlorate of neurine, yellow microscopic needles, which dissolve sparingly in cold, easily in boiling water, and separate therefrom in long distinct prisms. — When heated it melts to a brown liquid, which solidifies in the crystalline form on cooling (Baeyer). This salt likewise resembles the corresponding salt of sincaline (Claus & Keesé).

			Baeyer.	Wurtz. mean.
10 C	60	13·55	13·46	13·50
N	14	3·16		3·34
14 H	14	3·16	3·27	3·25
2 O	16	3·61		
Au	197	44·43	44·95	44·90
4 Cl	142	32·09		
$C^{10}NH^{13}O^{2},HCl,AuCl^{3}$	443	100·00		

Hydrochlorate of neurine does not precipitate *platinocyanide of potassium* (Diakonow) *Zeitschr. f. Chem.* [2] 4, 69.

Acetyl-neurine.

BAEYER. *Ann. Pharm.* 142, 325.

Hydrochlorate of neurine treated with chloride of acetyl deliquesces to a syrup, from whose aqueous solution, prepared after the excess of acetyl chloride has been driven off, auric chloride throws down granules and nodular groups of prisms of the chloroaurate. Chloride of platinum also forms with this solution an easily crystallising sparingly soluble compound.

	Crystals.		Baeyer. *mean.*
14 C	84	17·32	17·14
N	14	2·89	
16 H	16	3·30	3·40
4 O	32	6·59	
Au	197	40·62	40·10
4 Cl	142	29·28	29·45
$C^{10}NH^{12}(C^{4}H^{3}O^{2})O^{2},HCl,AuCl^{3}$	485	100·00	

Vitellin.

BENCE-JONES. *Ann. Pharm.* 40, 65.
DUMAS & CAHOURS. *N. Ann. Chim. Phys.* 6, 385; *Berzel. Jahresber.* 23, 590.
GOBLEY. *N. J. Pharm.* 9, 8; 11, 5, 81, 161 and 409; 12, 5; *Pharm. Centr.* 1847, 584; *Berzel. Jahresber.* 26, 914.
BAUMHAUER. *Scheik. Onderzoek.* 3, 272; *Berzel. Jahresber.* 27, 674.
NOAD. *Chem. Gaz.* 1847, 409; *Lieb. Kopp. Jahresber.* 1847 and 1848, 841.
VALENCIENNES & FRÉMY. *Compt. rend.* 38, 460; *Lieb. Kopp. Jahresber.* 1854, 684.
DENIS. *Mémoire sur le sang.* Paris, 1859, 185.
HOPPE-SEYLER. *Tubinger medic. Unters.* 1, 215.

1. The vitellin of Bence-Jones, Dumas & Cahours, and Noad, is hard-boiled yolk of egg, which has been exhausted with ether, or with ether and alcohol. It reacts like albumin with fuming hydrochloric acid.

	Bence-Jones. mean.	Dumas & Cahours. mean.	Noad. mean, at 100°.
C	52·90	51·60	53·96
H	7·43	7·22	7·79
N	13·47	15·02	12·81

Bence-Jones's contained vitellin 9·02, that of Dumas & Cahours, 3·6 to 4·48 p. c. ash; Noad alone determined the sulphur, which he found amount to 1·67 p. c.

2. v. Baumhauer frees yolk of egg from albumin; triturates it with water; coagulates the vitellin by mixing the filtrate with alcohol; and washes with alcohol and ether. Vitellin thus prepared contains 4·6 p. c. phosphate of lime, no phosphorus in organic combination. For purification it is dissolved in acetic acid, for which several hours' boiling is required, and precipitated by ammonia; it is thereby obtained as a yellowish-white precipitate, which must be washed with water till the water runs away turbid, then with alcohol and ether.

Vitellin purified with acetic acid is nearly insoluble in water, whether cold or boiling, but diffuses itself therein and runs through the filter. It dissolves in dilute mineral acids, swells up in acetic acid, and dissolves when the liquid is diluted and heated. From the acetic solution, potash throws down a precipitate soluble in excess, ferrocyanide of potassium a yellow precipitate; the same solution is precipitated by basic lead acetate, mercuric nitrate, and platinic chloride, but not by mercuric chloride or silver nitrate. This vitellin contains at 120°, 52·72 p. c. C., 7·09 H., 15·47 N.; the proportion of sulphur was estimated by Baumhauer, probably too low, at 0·47 p. c.

3. Valenciennes & Frémy prepare their vitellin by treating the yolk of hens' eggs with a large quantity of cold water, whereby albumin is dissolved and vitellin precipitated, and wash the precipitate with water, alcohol and ether. Vitellin dissolves in alkalis; it does not decompose peroxide of hydrogen.

4. Gobley obtains either coagulated vitellin by drying yolk of egg on shallow plates, and boiling it with alcohol; or soluble vitellin, by triturating the yolk with water, and diluting the emulsion thus obtained with a large quantity of water, whereupon the emulsive yolk is precipitated and the vitellin dissolves. — This solution becomes opalescent at 60°, and at 73° to 76° the vitellin separates in flocks. It is coagulated by sulphuric and hydrochloric acid, but not by acetic, lactic, tartaric, or phosphoric acid, or by potash, soda, baryta, or lime. — The coagulated vitellin is colourless, swells up to a jelly in potash-ley, and then dissolves.

	Valenciennes & Frémy.		Gobley.
C	51·60	52·26	52·26
H	7·22	7·24	7·25
N	15·02	15·28	15·06

Gobley found also 1·17 p. c. sulphur, and 1·02 phosphorus; his vitellin contained 4·82 p. c. ash.

Vitellin is, according to Lehmann (*Handbuch.* viii, 282; *Lehmann's*

Physiological Chemistry, ii, 356) a mixture of casein and albumin. When yolk of egg is triturated with water, and exhausted with ether, and the coagulum is washed as long as the wash-water becomes turbid when heated, casein remains behind, while albumin passes into solution. Schwarzenbach (*Ann. Pharm.* 141, 64) dissolved the residue on the filter several times in carbonate of soda; precipitated with acids; boiled with glacial acetic acid, whereupon the precipitate became translucent and then dissolved; and obtained from this solution, with platinocyanide of potassium, a precipitate containing, on the average, 11·12 p. c. platinum, whilst the albuminous solution which ran away yielded a precipitate containing 5·49 p. c. platinum. From these results he likewise infers that vitellin is a mixture of casein and albumin.

When vitellin (how prepared?) is boiled for several hours with moderately dilute sulphuric acid, leucine, tyrosine, and aspartic acid are obtained, but no glutamic acid (Kreusler, *J. pr. Chem.* 107, 239).

When the portion of egg-yolk insoluble in water is dissolved in slightly acidulated water precipitated with hydrochloric acid, redissolved in water, and precipitated with platinic chloride, the precipitate contains 7·85 p. c. platinum. — From boiled egg-yolk which has been washed with alcohol, ether, and water, dissolved in soda-ley, precipitated with hydrochloric acid, and redissolved, a precipitate is obtained, containing 7·96 p. c. platinum (Commaille).

5. When yolk of egg is shaken up in a half-filled bottle with twice its volume of ether, till it has become colourless and the ether no longer takes up any fat, the ether then removed by decantation and by spreading out the exhausted egg-yolk on a porcelain plate at 30°—40°, and the yolk suspended in a 10 p. c. solution of common salt, it dissolves completely in the course of a few hours. The colourless liquid thus obtained is coagulated by alcohol and by heating, also by acids and by concentrated alkalis. Water throws down very fine flocks of unaltered vitellin, which is therefore insoluble in water; but dissolves in a 10 p. c. solution of common salt. The solution mixed with a few drops of alkali or alkaline carbonate, and then no longer precipitable by water, coagulates when heated to 70°—74°, on addition of alcohol or a very small quantity of acid (Denis).

6. When the solution in salt-water of egg-yolk exhausted with ether, as obtained by Denis's method, is precipitated by water, with addition of a few drops of acetic acid, the egg-yellow is obtained in its original state. But when this yellow substance is treated with alcohol at 30° to 40°, it is resolved into lecithine, which dissolves, and a residual albuminous substance identical with the vitellin of some chemists. This substance is free from phosphorus, contains 0·75 p. c. sulphur, and no longer dissolves in a 10 p. c. solution of salt.

Unaltered vitellin is not precipitated from its solution in salt-water by saturation with common salt. It dissolves in water containing $\frac{1}{10}$ p. c. hydrochloric acid, but the solution soon becomes turbid, from separation of lecithine.

This vitellin occurs in the egg-yolk probably of all animals, especially in caviare, from which it may be extracted by salt-water.

On the nuclear structures in the yolk of the hen's egg, see F. Miescher, *Med. Chem. Unters.* 1871, 502.

The ichthin, ichthulin, and emydin of Valenciennes & Frémy, and the crystals of aleurone, consist of vitellin, or bodies allied thereto, and are resolvable, like vitellin, into an albuminous substance and lecithine (Hoppe-Seyler).

Ichthin. — Forms the yolk-plates in the eggs of cartilaginous fishes, as of the ray, torpedo, and shark, and falls down when the egg-yolk is suspended in a large quantity of water; may be purified by washing with water, alcohol, and ether. — Ichthin forms transparent grains, which appear as rectangular plates when prepared from the egg-yolk of oviparous species, and as oval plates when obtained from that of viviparous species, but do not exhibit the optical properties of crystals. — Ichthin is insoluble in water, and does not become opaque even in boiling water. It dissolves in dilute phosphoric and acetic acids, in other acids only in the concentrated state, in hydrochloric acid without violet coloration. It is not perceptibly soluble in ammonia, dissolves slowly in potash- or soda-ley, not in alcohol or ether. Contains 51·0 p. c. C., 6·7 H., 15·0 N., 25 4 O., and 1·9 P., no sulphur, and leaves no ash when burned. (Valenciennes & Frémy, *Compt. rend.* 38, 480; *Jahresber.* 1854, 684). On yolk-plates, which may be regarded as crystals, see Radlkofer (*Zeitschr. fur wissensch. Zoologie von Siebold & Kölliker* 9, 529).

Ichthidin and *Ichthulin.* — Whilst the ripe eggs of the carp and other bony fishes contain exclusively an albuminous liquid holding in suspension a phosphoretted fat, the same eggs in course of development contain granules resembling ichthin, but consisting of ichthidin, which is soluble in water, and consequently has not yet been isolated. When the solution obtained by triturating young carp's eggs with a little water, and merely rendered turbid by fat, is diluted with a larger quantity of water, ichthulin separates as a ropy syrup. By washing with alcohol and ether, this substance is obtained as a solid pulverulent mass, which dissolves in acetic and phosphoric acids, and without violet coloration in hydrochloric acid. Ichthulin contains 52·5 to 53·3 p. c. C., 8·0 to 8 3 H., 15·2 N., 0·6 P., 1·0 S., and 22·7 O. (Valenciennes & Frémy, *Compt. rend.* 38, 528; *Jahresber.* 1854, 684).

Emydin. Occurs in the eggs of tortoises, and is separated from the yolk by washing with water, alcohol, and ether. — White, translucent, round or oval grains, harder and heavier than ichthin. Dissolves in hydrochloric acid, without violet coloration; swells up in acetic acid without dissolving; and dissolves quickly in very dilute potash-ley. Contains, to 1 p. c. ash, 49·4 p. c. C., 7·4 H., 15·6 N., 27·6 O. and P. (Valenciennes & Frémy, *Compt. rend.* 38, 570; *Jahresber.* 1854, 684).

On Hartig's *Aleurone* or *Klebermehl* (*Botan. Ztg.* 1855, 881; 1856, 257; *Jahresber.* 1858, 491), see Maschke (*J. pr. Chem.* 74, 436; *Chem. Centr.* 1858, 864; *J. pr. Chem.* 79, 148); v. Holle (*N. Jahrb. Pharm.* 11, 338; 12, 65; Schmidt's *Jahrb.* 101, 281); Radlkofer (*Ueber kryst. proteïnart. Körper*, Leipzig, 1859; *Jahresber.* 1860, 329); F. Cohn (*J. pr. Chem.* 80, 129; *Jahresber.* 1860, 530).

Hæmoglobin.

HOPPE-SEYLER. *Archiv. fur pathol. Anat.* 23, 446; *Chem. Centr.* 1862, 170; *Jahresber.* 1862, 535.—*Archiv. für pathol. Anat.* 29, 233, and 597; *Chem. Centr.* 1864, 582; *Krit. Zeitschr.* 7, 341; *Jahresber.* 1864, 653.—*Zeitschr. f. Chem.* [2], 514; *Jahresber.* 1865, 771.—*Zeitschr. f. Chem.* [2], 1, 214; *Anal. Zeitschr.* 3, 432; *Chem. Centr.* 1865, 771; *Jahresber.* 1865, 665.—*Zeitschr. f. Chem.* [2], 1, 218; *Analyt. Zeitschr.* 3, 440; *Chem. Centr.* 1865, 776; *Jahresber.* 1865, 668.—*Tubinger medic.-chem. Unters.* Berlin, 1866 to 1868, 1, 169, and 366.—*Deutsche-chem. Gesellsch.* 3, 229.

Hæmatoglobin, Hæmatocrystallin. Colouring matter of Blood, or *Blood-red. Blood crystals. Cruorin of Denis and Stokes.*—Crystals from blood were obtained by Funke (*Zeitschr. f. rationelle Medicin,* neu Folge, 2, 199 and 288), and Kunde (*ibid.* 2, 271), and were prepared in larger quantity by Lehmann; but their preparation in the pure state was first effected by Hoppe-Seyler, who also determined their relation to hæmatin. See also the experiments of Funke and of Lehmann (*Handbuch,* viii, 135).

For older experiments on the preparation of the colouring matter of blood, see Fourcroy and Vauquelin (*Scher. J.* 8, 37); Brande (*Schw.* 18, 382); Vauquelin (*Ann. Chim. Phys* 1, 9); Engelhardt (*Kastn. Arch.* 6, 337); L. Gmelin (*Die Verdauung von. Tiedemann u. Gmelin*); Sanson (*Berzel. Lehrbuch* 3 Aufl. 9, 68), and below.—Berzelius (*Lehrbuch* 3 Aufl. 9, 71), and Simon (*N. Br. Arch.* 18, 35; *J. pr. Chem.* 22, 112) spoke of blood-red (Simon's hæmato-globulin) as a compound of hæmatin and globulin.—The presence of iron in the blood was first demonstrated by Lemery.

Occurrence. In the blood, probably, of all vertebrate animals. In man and in the dog it forms, with exception of mere traces of other substances, the sole constituent of the red corpuscles; in those of many other mammals and of birds, it occurs associated with albuminous substances.—The red serum of the earth-worm contains the same hæmoglobin as the blood of vertebrate animals (Nawrocki, *Chem. Centr.* 1867, 692).

Preparation. Blood freed from fibrin by beating it for ten minutes, is strained through linen which has been washed and dried again, and the filtrate is mixed with ten times its volume of a mixture of 1 vol. saturated solution of common salt and 9 to 19 vols. water. The mixture thus prepared is left to itself at or below 0°, till the blood-corpuscles have sunk to the bottom; and these corpuscles are purified by decanting the supernatant liquid, stirring them up with a weak solution of common salt, decanting, and repeating these operations once or twice. The pulp of blood-corpuscles free from serum thus obtained, is shaken up with a little water and 4 to 10 vols. ether; the whole is left at rest for some hours; the ether, holding in solution cholesterin and lecithine is poured off from the red aqueous solution; and this solution is cooled, whereupon it coagulates to a crystalline pulp. The crystals are dissolved in water of 30° to 35°, and the filtrate is quickly cooled to 0°, agitated with air, mixed with $\frac{1}{4}$ vol. alcohol of 80 p. c., again shaken with air, and then left to itself for a day or two at a temperature of $-5°$ to $-10°$. The crystals thereby obtained are washed with a cooled mixture of 1 vol. alcohol of 80 p.c. and 4 vols. water, and recrystallised in the manner above described (Hoppe-Seyler).

Or a mixture of 1 vol. defibrinated blood, 1 vol. water, and $\frac{1}{4}$ vol. alcohol is left to itself at 0° for 24 hours; the precipitate which separates is collected on a filter, pressed, and dissolved in the smallest possible quantity of water at 25—30°, and the solution mixed with a quantity of alcohol amounting to one-fourth its volume, is cooled to between − 10° and − 20° (Hoppe-Seyler).

The blood of dogs, guinea-pigs, hedge-hogs, and rats yields crystals of hæmoglobin when the corpuscles are merely shaken up with ether and water; that of birds only when, after this treatment, it is mixed with $\frac{1}{4}$ vol. alcohol, shaken with air, and cooled.—The separation of the hæmoglobin crystals and their recrystallisation succeeds only at a uniform temperature below 0°; but strongly cooled alcohol added to solutions of hæmoglobin at temperatures below 0°, throws down amorphous hæmoglobin, which remains amorphous even after solution in water and precipitation with alcohol (Hoppe-Seyler).

The blood of men, oxen, sheep, pigs, and rabbits does not yield crystals of hæmoglobin, but an amorphous precipitate, which is not obtained in the crystalline state, even after solution in warm water, and mixture with alcohol. To separate this amorphous hæmoglobin, the blood-corpuscles are agitated with water and ether; the ether is decanted after some hours; basic lead acetate is dropped into the red aqueous solution as long as a precipitate is formed; the excess of lead is removed by carbonate of potash; and pulverised carbonate of potash is added to the ice-cold filtrate till the hæmoglobin separates in light red flocks.—It is filtered off at 0°, and washed with a nearly saturated solution of carbonate of potash, but cannot be obtained quite free from this salt (Hoppe-Seyler).

The preparation of hæmoglobin crystals requires either an addition of water to bring out the contents of the corpuscles into the blood-liquid, or the destruction of the corpuscles by keeping the blood and allowing it to freeze. But too large an addition of water gives rise to decomposition of the hæmoglobin into hæmatin and paraglobin. Thus guinea-pig's blood diluted with half its volume, or at most an equal volume of water, yields an abundant crystalline sediment; but with a larger addition of water the crystals are accompanied, or finally replaced, by granules of paraglobin. The separation of crystals is promoted by agitation with small quantities of alcohol or ether, by dissolution of anhydrous sulphate of soda in the liquid, whereby its power of dissolving hæmoglobin is diminished; also by passing carbonic acid through the liquid, or by adding a very small quantity of acetic, hydrochloric, or sulphuric acid, whereby the alkali of the blood-water is neutralised. See especially A. Schmidt (*Virch. Arch.* 29, 14; *Müller's Arch.* 1862, 435); further, W. Kuhne, (*Medic. Centralblatt.* 1863, No. 53; *Lehrb.* 197).

Blood mixed with ether does not putrefy, but yields crystals after some weeks: hence to prepare these crystals (for microscopic observation) blood may be defibrinated, freed from serum, frozen, and mixed with ether after it has thawed (Zawarykin, *Wein. Acad. Ber.* 51, 151; *Analyt. Zeitschr.* 5, 263).

Properties. Hæmoglobin in the moist state forms a light cinnabar-red crystalline mass, and after drying below 0°, a light brick-red powder. If the temperature rises above 0° during the desiccation, the hæmoglobin becomes dark red, or nearly black, and partly decomposes (Hoppe-Seyler). The crystals are mostly rhombic prisms, but in the blood of certain animals, tetrahedrons tables, or rhombohedrons likewise occur (*Handbuch*, viii, 136). The blood of hedgehogs yields hexagonal crystals; that of guinea-pigs yields rhombic tetrahedrons (v. Lang). The crystals from dog's blood are 2 lines long and $\frac{1}{8}$ of a line thick (Hoppe-Seyler).

The crystals must first be dried at 0° in a vacuum, then, when the weight has become constant, at 100°—120°. At the latter temperature they lose from 3 to 9·4 p. c. water, according to their origin, crystals from dog's blood giving off 3 to 4, those from goose blood 7, those from guinea-pig's blood 6, and those from hedgehog's blood 9·4 p. c. water.

	C. Schmidt.	Hoppe-Seyler. *Dried at* 100°; *mean.*			
	Dried, mean.	*Dog.*	*Goose.*	*Guinea-pig.*	*Hedgehog.*
C	53·64	53·85	54·26	54·12	54·09
N	16·19	16·17	16·21	16·78	16·09
H	7·11	7·32	7·10	7·36	7·39
S	0.66	0·39	0·54	0·58	0·40
Fe	0·43	0·43	0·43	0·48	0·59
O	21·02	21·84	20·69	20·68	21·44
	99·05	100 00	99 23	100·00	100·00

C. Schmidt's analyses are from A. Böttcher's work (*Ueber Blutkryst.* Dorpat, 1862, and *Virch. Arch.* 29, 599); his crystals still contained 0·95 p. c. phosphates. Hoppe's hæmoglobin from goose blood also contained 0·77 p. c. phosphoric acid; that from the blood of other animals contained none. But even in these the composition of the hæmoglobin is not exactly the same, that from guinea-pig's blood, for example, containing more nitrogen. To these differences in the composition of oxy-hæmoglobin from various sources correspond small differences in the intensity of light-absorption and in solubility (Hoppe-Seyler).

Kühne (*Lehrb.* 193) found no sulphur, but, according to Hoppe-Seyler, the presence of this element is demonstrated by the production of albuminous substance in the decomposition of hæmoglobin.

Oxyhæmoglobin.—Hæmoglobin crystals contain, in the moist state, and when suspended in water, less abundantly when they have been pressed or dried at 0°, a quantity of loosely-combined oxygen, which may be expelled by exhaustion with the air-pump, or replaced by carbonic oxide. 100 gr. of the crystals, dissolved or suspended in water gave in a vacuum 120 to 130 cub. cent. oxygen at 0° and 1 metre pressure; part of the oxygen appears, however, to remain behind in a state of fixed combination, or to be converted into carbonic acid (Hoppe-Seyler; Preyer. *Medic. Centr.* 1866, No. 21).

A solution of hæmoglobin is capable of fixing a quantity of oxygen equal to that contained in an equal volume of blood, whence it may be inferred that all or nearly all the oxygen of the blood is combined with hæmoglobin (Dybkowsky, *Tubinger medic. Untersuch.* 1, 117).

Oxyhæmoglobin decomposes when its *aqueous solution is boiled*, when its hot solution is mixed with *alcohol*, or when it is treated with *acids* or *alkalis*, yielding hæmatin, albuminous bodies, traces of formic acid, butyric acid, and amorphous nitrogenous bodies (Hoppe-Seyler). The products of decomposition remain in solution after the undecomposed hæmoglobin has been precipitated by pulverulent carbonate of potash; the albuminous substances are precipitated, together with a little hæmatin, on agitating the aqueous solution with ether. In a solution of common salt, they swell up as a gelatinous mass, without dissolving, give up a soluble portion to very dilute hydrochloric acid, and shrink together in boiling water (Hoppe-Seyler).

When oxyhæmoglobin is freed from loosely combined oxygen by passing hydrogen or carbonic acid through it, and mixed, apart from the air, with de-aërated alcohol which has been either acidulated with sulphuric acid, or mixed with a little caustic potash, the liquid acquires a fine purple-red colour, and deposits a colourless precipitate, or if alkaline alcohol has been used, a light purple-red precipitate, of albumin. The colouring matter which remains dissolved is neither hæmatin—which is obtained only when oxyhæmoglobin is employed, or when air has access to the liquid—nor reduced hæmatin, but *hæmochromogen.* Its solutions exhibit four absorption-bands, the acid alcoholic solution two narrow bands between C and D, a broader band between D and E, and a diffused band between *b* and F. The alkaline solution exhibits a faint absorption-band before D; a very strong sharp band midway between D and E; a third, extending from E to *b;* and a fourth, broad and ill-defined, which begins behind *b* and reaches nearly to F (Hoppe-Seyler).

The decomposition of hæmoglobin begins even during the drying up of its aqueous solution, or when that solution is left to itself, and the more easily as the temperature is higher; moist crystals lying exposed to the air acquire a dingy dark-red colour. The product thus formed, Hoppe's *Metahæmoglobin*, yields hæmatin with alcoholic acid, even in absence of oxygen.

In presence of *metallic chlorides*, *acetic acid* produces from oxyhæmoglobin, instead of hæmatin, crystals of hydrochlorate of hæmatin, of which 3·86 pts. are obtained from 100 pts. hæmoglobin, whereas calculation, based upon the amount of iron in the two bodies, requires 4·87 pts. (Hoppe-Seyler).

Dry hæmoglobin dissolves at 5° in 50 pts. of *water*, more easily in aqueous albumin or aqueous carbonate of soda; its separation from these solutions is facilitated by a stream of carbonic acid (Hoppe-Seyler).

When *cupric sulphate* is dropt into aqueous blood-red, the resulting precipitate disappears on agitation, then becomes permanent, and is obtained of a brown-green colour if the metallic salt is in excess. When blood-red is dropt into excess of cupric sulphate, the liquid becomes green without precipitation.—The precipitate decomposes during washing, with formation of soluble compounds; when produced with excess of cupric sulphate, it contains sulphuric acid and cupric oxide in the proportion of the neutral salt; with excess of blood-red there is obtained, besides a brown precipitate, a filtrate containing a large quantity of free sulphuric acid. The copper in the precipitates cannot be detected till the organic matter has been destroyed (C. G. Mitscherlich. *Pogg.* 40, 126). See also F. Rose (*Pogg.* 28, 132).

With *mercuric chloride*, blood-red forms a red precipitate, which dissolves in water, after the mercuric salt has been washed out (F. Rose).

Aqueous hæmoglobin is not precipitated by *nitrate of silver* (Lehmann); it is precipitated after 12 to 24 hours (Alex. Schmidt).

The loosely-combined oxygen imparts to hæmoglobin the faculty of absorbing with peculiar energy light of a certain degree of refrangibility: hence the spectrum which has passed through a solution of hæmoglobin exhibits dark bands, which are not obtained of similar character with other red colouring matters, or even with the products resulting from the decomposition of hæmoglobin (Hoppe-Seyler; Stokes, *Proc. Roy. Soc.* 13, 355; *Chem. Centr.* 1865, 412; *Jahresber.* 1865, 665, and 668).

A very dilute solution of blood in water exhibits in a layer 1 centimetre thick, two dark bands in the yellow and green, situated between the Fraunhofer lines D and E. The band corresponding to the less refracted light lies near the double line D; the second is somewhat farther from E; with a sufficiently dilute blood-solution, the breadth of the two is less than the spectral interval between E and *b*. With greater concentration or a thicker layer of the blood-solution, the breadth of the two absorption-bands increases, and almost wholly at the expense of the yellow-green light which separates the two bands from one another; and, finally, as the concentration is increased, the two bands unite into a dark, somewhat sharply-bounded field. At the same time the violet and blue gradually disappear, so that nothing is left of the spectrum but the green between E and *b*, and the red and orange as far as D, and with still greater concentration, only the red (Hoppe-Seyler).

The blood of different vertebrate animals, when thus examined, exhibits similar characters; the same absorption-phenomena are likewise observable in undissolved blood-corpuscles (Hoppe-Seyler).—On the estimation of hæmoglobin in blood by means of the spectroscope, see Preyer (*Ann. Pharm.* 140, 187; *Anal. Zeitschr.* 5, 414).

Arterial and venous blood exhibit the same two absorption-bands in the yellow and the green; but venous blood absorbs the light from C to near D more strongly than arterial blood (Hoppe-Seyler).

Reduced Hæmoglobin.—Oxygen may be withdrawn from oxyhæmoglobin or from blood by the commencement of putrefaction in blood from the arteries, or by the addition of reducing substances to the blood. This change is produced by prolonged keeping of extract of blood in closed vessels (Stokes), by heating the blood-solution to 40°—50° by itself, or with a drop of ammonia (Hoppe-Seyler); by alkaline sulphides, zinc, iron, ammoniacal solutions of ferrous, cuprous, or stannous oxide. The two absorption-bands then disappear and are replaced by a single band situated midway between D and E. As the hæmoglobin itself is not necessarily destroyed in these reactions, the absorption-bands of the oxygenated hæmoglobin or oxy-hæmoglobin reappear in certain cases after agitation with air (Stokes; Hoppe-Seyler). Oxyhæmoglobin is not reduced by grape-sugar or tartaric acid (Hoppe-Seyler).

Hæmoglobin free from oxygen is likewise crystallisable; the crystals obtained when the air is excluded as completely as possible are dark brown-red, belong also to the rhombic system, and are more soluble than the oxygenated crystals (W. Kühne, *Virch. Arch.* 34, 123). Hoppe-Seyler did not succeed in obtaining crystals by mixing aqueous hæmoglobin deoxidised by passing hydrogen through it, with alcohol at 0°, or by drying it over oil of vitriol; but on admission of air to the liquid, crystallisation took place rapidly.

A solution of reduced hæmoglobin concentrated to a certain degree, transmits only the red light from the beginning of the spectrum to a little beyond C; on dilution, the following appearances are observed:—1. The spectrum becomes visible further towards the line D, and green light appears between *b* and F.—2. The broad, ill-defined band from D to *b* becomes broader, without separating into two bands; at the same time the spectrum becomes brighter towards the blue.—3. There remains a broad, ill-defined absorption-band between D and E (Hoppe-Seyler).

Blood diluted with water becomes dark purple-red when it is made ammoniacal and mixed with ferrous tartrate; it then exhibits, instead of the two absorption-bands, a single band less sharply defined, and as the thickness of the layer is increased, ultimately transmits only the blue a little behind F, whereas in the original solution, the green between E and *b* disappears last (Stokes).

Blood mixed with alkaline *stannous oxide* exhibits, after several weeks, the original spectrum of reduced hæmoglobin (Nawrocki).

Acetic or *tartaric acid* converts the red colour of blood-solution into brown-red, whereupon, instead of the original absorption-bands, another system of bands makes its appearance, belonging to the decomposition-products of hæmoglobin (Stokes). In the decomposition of hæmoglobin by acids, absorption-bands appear in the neighbourhood of the line C, their position varying according to the acid employed. At the same time the loosely combined oxygen disappears, being employed in effecting the decomposition of the hæmoglobin or other constituents of the blood. The same effect is produced by continued passage of carbonic acid gas (Hoppe-Seyler).

Peroxide of hydrogen does not alter the spectrum of blood (Schönbein, *Jahresb.* 1867, 808). Acid blood turned brown by peroxide of hydrogen exhibits only the bands of the acid solution of hæmatin (Huizinga, *Analyt. Zeitschr.* 8, 234).

Solutions of hæmoglobin free from oxygen are not decomposed by continued passage of *hydrosulphuric acid gas*, or only after several days; neither does the decomposition take place quickly when ammonia is likewise added. But when hydrosulphuric acid is passed through an aqueous solution of oxy-hæmoglobin, the oxygen is slowly separated from the hæmoglobin. In an ammoniacal solution the decomposition stops at this point, but neutral solutions suffer further alteration, in consequence of which the solution acquires a dirty green colour, and an absorption-band appears in the red between C and D. The appearance of this band is not determined by the formation of hæmatin, as shown by the spectrum of the solution mixed with ammonia, but probably by the formation of a sulphur-compound, either of hæmatin or of hæmoglobin. By further passage of hydrosulphuric acid gas, a body is formed, having an olive-green colour in thin layers, brown-red in thicker layers, and a mixture of sulphur and an albuminous body is separated; the filtered liquid neither exhibits distinct absorption-bands nor yields crystals, but when left to evaporate in a vacuum, leaves an amorphous residue rich in sulphur, which exhibits the original amount of iron in hæmoglobin (Hoppe-Seyler, Lewisson, *Virch. Arch.* 36, 15).

Small quantities of commercial *hydrosulphate of ammonia* act but slowly on oxyhæmoglobin; larger quantities reduce it almost instantaneously. When 1 vol. hydrosulphate of ammonia is added to 3 vol. solution of oxyhæmoglobin, the absorption-band in the red near C first appears, and afterwards two bands, which do not disappear even after the solution has been left to itself for a day or two (Nawrocki, *Chem. Centr.* 1867, 689).—According to Hoppe-Seyler (*Tubinger Medic. Unters.* 1, 299) the two bands belong to reduced hæmatin; he himself was unable to obtain them at ordinary temperatures with hydrosulphate of ammonia.

Liver of sulphur dissolves without turbidity in cold aqueous oxyhæmoglobin, and develops in the first instance the broad absorption-band of deoxidised hæmoglobin. Next there appear two black sharply defined bands, one between D and E, the other between D (near E) and *b*. The liquid remains clear on boiling, and exhibits while hot a shady spectrum without distinct bands, which, however, reappear on rapid cooling (Preyer, *Chem. Centr.* 1867, 692). In this case also the two bands belong to reduced hæmatin produced by the free alkali. When aqueous hæmoglobin mixed with hydrate and hydrosulphate of potassium is heated to the boiling point, the solution acquires a dark colour, but does not exhibit absorption-bands till it has cooled (Hoppe-Seyler).

When *phosphoretted hydrogen* is passed through aqueous oxyhæmoglobin, or through dilute oxygenated blood, the liquid acquires a darker yellow-brown colour, becomes less transparent, and exhibits the absorption-spectrum of oxyhæmoglobin less distinctly than before; moreover, neither the spectrum nor the colour can be restored by agitation with air.—A continued stream of phosphoretted hydrogen renders the solution greenish-brown and more turbid, without developing the spectrum of reduced hæmoglobin, or of hæmatin. After some hours there is formed a grey precipitate containing blood-corpuscles free from pigment. These alterations are more striking when the blood is diluted with a mixture of 1 pt. alcohol and 4 pts. water; in undiluted defibrinated blood they take place slowly, the blood then assuming a cherry-red-brown colour (Koschlakoff & Popoff, *Chem. Centr.* 1867, 696).

Arsenetted and *antimonetted hydrogen* alter oxygenated, but not deoxygenated hæmoglobin, without separation of arsenic or antimony (Lewisson, *Virch. Arch.* 36, 15).

Hæmoglobin with Carbonic Oxide.—When aqueous hæmoglobin is shaken up with carbonic oxide gas, the whole of the oxygen is expelled and an equal volume of carbonic oxide absorbed, the solution at the same time acquiring a light purple-red colour.—When carbonic oxide is passed for some minutes through aqueous defibrinated blood, or through an aqueous solution of blood-corpuscles, or of oxyhæmoglobin, the liquid then cooled to 0°, mixed with one-fourth its volume of 80 p. c. alcohol, and left to itself for 24 hours at or below 0°, crystals of the compound of carbonic oxide and hæmoglobin are obtained.—They are bluish-red four-sided prisms, apparently isomorphous with the crystals of oxyhæmoglobin, and larger than the latter.

The crystals dissolve in water less easily than oxyhæmoglobin, forming a darker and more bluish liquid, the absorption-spectrum of which, though very much like that of oxyhæmoglobin, is nevertheless distinguished by the following characters: 1. The carbonic oxide compound absorbs blue light much less than oxyhæmoglobin; 2. In the spectrum of the carbonic oxide compound the absorption-bands between the lines D and *b* are situated nearer to *b*; 3. Concentrated solutions of the carbonic oxide compound absorb the least refrangible red rays less than similar solutions of oxyhæmoglobin.

The moist crystals placed in a vacuum at 90° to 100°, give off part of the absorbed carbonic oxide, amounting to 10·2 cub. cent. at 0° and 1 metre pressure, for 100 gr. of the dry carbonic oxide compound of hæmoglobin, less, therefore, than one-tenth of the quantity absorbed. Neither the passage of indifferent gases, such as carbonic acid, nor the addition of hydrosulphate of ammonia, ammonio-ferrous tartrate, stannous tartrate, or ammonio-cuprous chloride, produce any immediate alteration in the colour, or in the absorption-spectrum. — Oxygen also does not act immediately, but produces carbonic acid after long contact (Hoppe-Seyler, *Tubinger Medic. Unters.* 1, 201. — Dybkowsky, *ibid.* 1, 117).

Hydrosulphuric acid does not alter the carbonic oxide compound of hæmoglobin apart from the air, but in contact with air it acts in the same manner as on oxyhæmoglobin (Lewisson, *Virchow's Arch.* 36, 15). — Potash-liver of sulphur causes the spectrum of the carbonic oxide compound of hæmoglobin to disappear only when that compound is heated to boiling with a large quantity of liver of sulphur; the spectrum which appears on cooling resembles that of oxyhæmoglobin after similar treatment. The same effect is produced by a large excess of hydrosulphate of ammonia, which, however, causes the solution to coagulate (Preyer, *Chem. Centr.* 1867, 692). See also Nawrocki, (*Chem. Centr.* 1867, 690). — Phosphoretted hydrogen acts on the carbonic oxide compound of hæmoglobin in the same manner as on oxyhæmoglobin (Koschlakoff & Popoff).

Hæmoglobin with Nitric Oxide. When nitric oxide gas is passed through arterial blood or aqueous oxyhæmoglobin, the absorption spectrum of the oxyhæmoglobin remains unaltered, excepting that it becomes somewhat fainter (Hoppe-Seyler). In this reaction the oxyhæmoglobin is first deprived of oxygen, and then unites with the excess of nitric oxide, forming a compound whose spectrum resembles that of oxyhæmoglobin (Hoppe-Seyler). The nitric oxide compound of hæmoglobin is obtained by passing nitric oxide into deoxygenated blood, which then acquires a fine crimson colour, or into the aqueous solution of the carbonic oxide compound, the reaction in this case not being attended with any alteration of volume. When oxygenated blood is agitated with baryta-water and nitric oxide gas, it becomes darker-coloured, from abstraction of oxygen, when a small quantity of nitric oxide has been taken up, but recovers its fine bright red colour by absorption of a larger quantity. — The compound of nitric oxide and hæmoglobin yields crystals isomorphous with those of oxyhæmoglobin; it is not decomposed by hydrosulphate of ammonia (L. Hermann, *Muller's Archiv.* 1865, 469; *Chem. Centr.* 1865, 1124. — Hoppe-Seyler, *Tubinger medic.-chem. Unters.* 1, 204). — The latter discovers some peculiarities in the absorption spectrum of the nitric oxide compound of hæmoglobin.

Nitrites colour arterial blood chocolate-brown, and greatly weaken the absorption-bands of oxyhæmoglobin; on the other hand a new band makes its appearance, coinciding with that of an acid solution of hæmatin. Hydrosulphate of ammonia and ferrous salts restore the spectrum of oxyhæmoglobin and then exert a reducing action. The nitrites of soda, potash, silver, and amyl, unite with oxyhæmoglobin, forming crystals which contain variable quantities of hæmoglobin (Gamgee, *Proc. Roy. Soc.* 16, 339; *J. pr. Chem.* 105, 287).

Hydrocyanate of Hæmoglobin. Hæmoglobin to which hydrocyanic acid has been added crystallises apparently without alteration, but exhibits, even after several recrystallisations and drying in a vacuum, an amount of hydrocyanic acid recognisable by distillation with dilute sulphuric acid. — The crystals are more permanent than those of oxyhæmoglobin, and exhibit the absorption-spectrum of that substance quite unaltered. In this case also, hydrosulphate of ammonia (or ammonio-ferrous tartrate) causes the two absorption-bands to disappear, and develops the band of reduced hæmoglobin (Hoppe-Seyler, *Tubinger medic. Unters.* 1, 206). — If the liquid be now heated, it becomes turbid, and exhibits two absorption-bands resembling those of the carbonic oxide compound of hæmoglobin, but situated nearer to the violet; on passing oxygen through the liquid, the spectrum of reduced hæmoglobin first appears, and then for a while that of oxyhæmoglobin (Preyer).

Aqueous *cyanide of potassium*, either dilute or concentrated, does not alter the optical characters of oxyhæmoglobin in the cold, but on heating the solution to the temperature of the body, it exhibits a yellowish glimmer and a broad absorption-band, somewhat nearer to the violet than that of reduced hæmoglobin; after agitation with air, it does not exhibit the spectrum of oxyhæmoglobin (Preyer). These appearances are due to the formation of hæmatin; they are produced even in the cold when hæmoglobin decomposed with caustic potash, or alkaline hæmatin, is decomposed by cyanide of potassium (Nawrocki, *Chem. Centr.* 1867, 695). — A solution of hæmoglobin warmed with cyanide of potassium, and then mixed with hydrosulphate of ammonia, exhibits a spectrum with two bands like that of the carbonic oxide compound of hæmoglobin, but after agitation with air it exhibits the spectrum of reduced hæmoglobin (Preyer, *Chem. Centr.* 1867, 693).

Blood containing prussic acid assumes a dark brown colour on addition of *peroxide of hydrogen*, even if the quantity of prussic acid present is very small, and exhibits an absorption-spectrum in which the red alone remains, but the absorption-bands of hæmoglobin are wanting. These phenomena do not occur when peroxide of hydrogen is first added to the blood and prussic acid afterwards (Schönbein, *N. Repert. Pharm.* 16, 605; *Jahresb.* 1867, 807). See also L. A. Buchner (*N. Repert. Pharm.* 17, 534; *Annlyt. Zeitschr.* 8, 108). Other acids also, when added in sufficient quantity to produce acid reaction, cause blood to turn brown after addition of peroxide of hydrogen; but in presence of prussic acid the following peculiarities are observed:—

a. Blood containing cyanide of potassium and turned brown by peroxide of hydrogen still exhibits, after 27 hours, the spectrum of oxyhæmoglobin, and after acidulation, the absorption-band of an acid hæmatin-solution in C. With potash after 24 hours it appears but little altered, excepting that, together with the spectrum of the oxyhæmoglobin, the absorption-band of alkaline hæmatin becomes faintly perceptible. When blood containing cyanide of potassium and turned brown by neutral peroxide of hydrogen, is mixed with ammonio-ferrous tartrate, the two bands disappear, and an absorption-band appears, narrower and lying near to the red end of the spectrum than that of reduced hæmoglobin (Huizinga, *Anal. Zeitschr.* 8, 233).

Cyanide of potassium causes the spectrum of the carbonic oxide compound of hæmoglobin to disappear, only when the liquid is heated considerably above 40°, the broad band of reduced hæmoglobin appearing at the same time. Hydro-sulphate of ammonia then produces a spectrum with two absorption-bands, which, by agitation with air, is converted either into that of reduced hæmoglobin or into that of the carbonic oxide compound of hæmoglobin. Hydrosulphate of ammonia acts also in the same manner on the carbonic oxide compound of hæmoglobin containing prussic acid, excepting that after agitation with air, the spectrum of oxyhæmoglobin is finally developed (Preyer, *Chem. Centr.* 1867, 694).

Acetylene unites with hæmoglobin, forming a compound which has the colour of the carbonic oxide compound, and is reduced by hydrosulphate of ammonia or ferrous tartrate (Bistrow & Liebreich, *Deutsche Chem. Gesellsch,* 1, 220).

Hæmatin.

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HOPPE-SEYLER. *Virchow's Archiv.* 29, 235 and 597; *Jahresber.* 1864, 653.—*Tübinger medic.-chem. Unters.* 1, 297 and 379; *Deutsche chem. Gesellsch.* 3, 229.

Hæmatosin of Chevreul and Lecanu.—*Blood-colouring matter* or *Blood-red* of the older chemists.

Produced from oxyhæmoglobin, together with albuminous substance, by the action of acids or alkalis.—Does not occur ready formed in the blood of vertebrate animals (Hoppe-Seyler).

Preparation. Hydrochlorate of hæmatin is produced by treating hæmoglobin with common salt and a large excess of glacial acetic acid; the crystals are dissolved in ammonia-water; the solution evaporated to complete dryness; and the residues heated for a considerable time to 130°, then exhausted with water and dried (Hoppe-Seyler.) — According to later statements of Hoppe-Seyler, hæmatin thus prepared has undergone partial alteration.

Lecanu drops sulphuric acid into defibrinated blood diluted with its own weight of water; suspends the resulting magma in alcohol; presses the residue; and boils it with alcohol containing sulphuric acid. The solution when quite cold is filtered, supersaturated with ammonia, again filtered and evaporated, after which the residue is washed with water, alcohol and ether, and dissolved in ammoniacal alcohol; the solution is filtered and evaporated; and the residue is washed.

Simon boils dry blood previously exhausted with boiling ether, with alcohol containing a little sulphuric acid; supersaturates the alcoholic tinctures with ammonia; leaves the sulphate of ammonia to settle; filters; distils off the greater part of the alcohol; evaporates; pulverises the residue; frees it from fat and hæmœphæin by ether, and then from admixtures soluble in water and in alcohol.

Berzelius separates the blood-corpuscles by mixing blood with strong solution of Glauber's salt; collects them; boils them with alcohol containing sulphuric acid; mixes them while still warm, with caustic ammonia or carbonate of ammonia; then filters and distils till only $\frac{1}{12}$ is left: the remaining liquid then deposits hæmatin, still requiring to be freed from fat by ether. The same process is adopted by Mulder.

v. Wittich agitates defibrinated blood with ether gradually added as long as it is taken up, and separates the lower cherry-red layer which forms after some minutes, from the supernatant coagulum by filtration. The resulting solution of hæmatoglobulin, or even fresh defibrinated blood, mixed with a very strong solution of carbonate of potash, deposits hæmatin as a dingy red clot, which is separated by filtration, dried completely at a temperature not exceeding 50°, pulverised, stirred up with absolute alcohol, and left in contact with it for a few days at a temperature below 50°. The liquid must be filtered in the cold, as otherwise globulin will remain dissolved; the alcoholic solution evaporated; the dry residue freed from fat by ether, then dissolved in water; and the hæmatin precipitated by acetic acid or by mineral acids.

Properties. Amorphous, dark greyish-blue, metallically lustrous mass, triturable to a brown powder, with brown streak (Hoppe-Seyler). Scentless and tasteless.

			Hoppe-Seyler.	Mulder.	
			at 130°.	*a.* *mean.*	*b.*
96 C	576	61·34	60·90 to 61·18	65·01	64·63
6 N	84	8·95	8·63	10·50	10·59
51 H	51	5·43	5·20 to 5·41	5·34	5·28
3 Fe	84	8·93	8·68 „ 8·83	6·66	6·45
18 O	144	15·35		12·49	13·05
$C^{96}N^6H^{51}Fe^3O^{18}$	939	100·00		100·00	100·00

a from ox-blood, *b* from sheep's blood. Lecanu found between 5·84 and 8·99 p. c. iron, mean 7·0 p. c.; Simon 7·97 p. c. Mulder's formula is $C^{44}N^3H^{22}FeO^6$. See also the analysis of Hæmin (p. 402). — In a further communication, Hoppe-Seyler (*Deutsche Chem. Gesellsch.* 3, 231) gives the formula $C^{68}N^4H^{34}Fe^2O^{10}$, which requires 64·35 p. c. C. (!), 8·83 N., 5·36 H., 8·83 Fe., and 12·62 O.

On account of the presence of hæmatin, extract of blood prepared with hot alcohol free from acid absorbs most strongly the violet light, and least strongly the extreme red of the spectrum to a little beyond the line B. Rather dilute solutions exhibit a well defined absorption-band covering the line C, and ultimately faint bands appear also in the green. Ammoniacal hæmatin in a solution containing 15 milligr. in 100 cub. cent., and a centimetre thick, exhibits an absorption-band between the lines C and D, nearer to C than to D. Stronger solutions transmit light only from a little before *a* to beyond B; on dilution, the beginning of the spectrum also shows itself to before A (Hoppe-Seyler).

From diluted blood mixed with acetic acid or other acids, an equal volume of ether takes up nearly all the hæmatin. This solution exhibits very distinctly three absorption-bands, one covering the line C, a second situated in the green before C, and a third, less sharply defined, between *b* and F (Nawrocki, *Chem. Centr.* 1867, 690).

Decompositions. 1. Hæmatin does not alter at 180°, but becomes carbonised without tumefaction at a stronger *heat*, and when burnt in the air, leaves 12·8 p. c. ferric oxide (Hoppe-Seyler). — 2. Strong *nitric acid* dissolves hæmatin with brown colour, giving off red vapours, and decomposing it (Lecanu; Mulder). Oxalic acid and a yellow resin are formed in this reaction (Hoppe-Seyler). Peroxide of *lead* decolorises the solution in alcohol containing sulphuric acid (Mulder).

3. The addition of reducing substances, especially of *ferrous tartrate* or *stannous oxide* to alkaline hæmatin alters the spectrum, developing two bands somewhat farther from D than in the spectrum of oxy-hæmoglobin; by agitation with air, the spectrum of brown oxidised hæmatin is reproduced (Stokes, *Phil. Mag.* [4], 28, 391; *Chem. Centr.* 1865, 412).

Hæmatin may also be reduced by sodium amalgam, zinc and soda-ley, tin and hydrochloric acid, hydrogen being taken up and the compound $C^{68}N^4H^{38}O^{12}$ produced; in strong solutions a resin is also formed. Tin and alcoholic hydrochloric acid quickly produce a purple body, which is precipitated with brown colour by water (Hoppe-Seyler).

¶ The action of tin and hydrochloric acid on hæmatin in presence of alcohol, is different accordingly as the hæmatin is fully dissolved or not. When a concentrated solution, or a solution containing excess of hæmatin is heated on the water-bath with tin, copper, or zinc, a purple-red solution is formed, and after some time a resinous dark violet precipitate. The solution is characterised by two dark absorption-bands between D and E. When hæmatin or hæmin-crystals dissolved in alcohol containing sulphuric acid are decomposed by hydrochloric acid and tin, and heated, a purple solution is formed, which also has a characteristic spectrum, exhibiting one band between D and E, another just before D, and another broad band between *b* and F, covering the latter line. When the evaporated solution is poured into boiling water, a brownish precipitate is formed soluble in alcohol; and the resulting solution yields a colouring matter which appears to have the composition $C^{68}N^{3}H^{49}ClO^{14}$. Analysis 63·57 p. c. C., 6·61 N., 7·68 H., 4·76 Cl.; calc. 63·10 p. c. C., 6·50 N., 7·58 H., 5·49 Cl., and 17·33 O. (Hoppe-Seyler, *Med.-chem. Unters.* 1871, 523). ¶

4. By prolonged boiling of hæmatin with moderately *dilute sulphuric acid*, leucine and tyrosine are obtained (Leyer & Köller. *Ann. Pharm.* 83, 532).

When a mixture of hæmatin with a large quantity of *oil of vitriol* is left to itself for several days and then diluted with water, the dark precipitate still contains about 5 p. c. ferric oxide, but a second treatment with oil of vitriol for several days removes almost all the iron. The resulting dark violet non-ferruginous hæmatin ($C^{68}N^{4}H^{36}O^{12}$, according to Hoppe-Seyler) contains at 120°, 68·85 p. c. C., and 5·92 H. (Mulder).

In this case Mulder appears to regard the product as free from sulphuric acid, whereas by the following process he obtained a compound containing sulphuric acid. Dried ox-blood drenched with a large quantity of oil of vitriol and left to itself for several days, swells up and continuously gives off sulphurous acid. — On carefully diluting with water, collecting that which separates, boiling it successively with alcohol containing sulphuric acid and with pure alcohol, and evaporating the extracts to dryness after addition of ammonia, there remains a mass which may be freed from foreign constituents by successive treatment with water, ether, and alcohol, and from which the non-ferruginous colouring matter may be extracted by alcoholic ammonia. The alcohol is distilled off from the dark red tincture and the residue is washed with water. It is red-brown, shining, lighter coloured than hæmatin; contains sulphuric acid and 57·6 p. c. C., 6·95 H., 12·42 N. — The same non-ferruginous hæmatin, with 4·42 p. c. SO^{3}, is obtained from the water used for diluting the blood which has been treated with oil of vitriol.

Lecanu also found that oil of vitriol and likewise sulphuric acid diluted with 6 pts. water, withdraw iron from hæmatin, but he did not obtain a product free from iron. Scherer (*Ann. Pharm.* 40, 30) prepared from a blood-clot treated with oil of vitriol, a deep blood-red alcoholic solution, which, when evaporated to dryness and incinerated, did not leave any iron. Hoppe-Seyler (*Tubinger medic.-chem. Unters.* 1, 300) describes the non-ferruginous product obtained from oil of vitriol and hæmatin as a sulphur-compound difficult to decompose. — The solution of hæmatin in oil of vitriol, or that of non-ferruginous hæmatin in dilute ammonia, exhibits a spectrum different from that of hæmatin, and further altered by hydrosulphate of ammonia or cyanide of potassium (Hoppe-Seyler). The spectrum of non-ferruginous hæmatin is likewise exhibited by solutions of hæmatin in alcohol containing a large excess of sulphuric acid (Koschlakoff & Popoff, *Anal. Zeitschr.* 6, 495).

When hæmatin is dissolved in alcohol containing a large quantity of sulphuric acid, the spectrum exhibits, instead of the absorption-band C, two new bands, namely a narrow band to the left of the line D, and a broader one between D and E, both belonging to the acid solution of non-ferruginous hæmatin. On supersaturating the solution with ammonia, there appear, in place of these two bands, four new ones, two broad and two narrow, the former situated to the right of D and the right of E, the latter in C and in the middle space between the two broader bands. Solutions of this kind are likewise obtained by dissolving hæmin in oil of vitriol and precipitating with water (Popoff, *Chem. Centr.* 1867, 698).

¶ *Hæmatoporphyrin and Hæmatolin.*—When a solution of hæmatin in oil of vitriol is filtered through asbestos, a beautiful purple-red solution is obtained, which gives a small dark absorption-band just before the line D, and another very sharply defined band between D and E. When this solution is mixed with water, the greater part is precipitated, the precipitate being increased by addition of alkalis to neutralisation. The alkaline aqueous solutions of the precipitate are characterised by a faint band between C and D, a similar faint band between D and E, nearer D, a dark band in the same interval but nearer E, and lastly, a very dark band between *b* and F. This substance, *hæmatoporphyrin*, is free from iron, and gives by analysis 68·42 p.c. C., 9·58 N., 6·07 H., 15·93 O., agreeing nearly with the formula $C^{68}N^4H^{37}O^{12}$, or $C^{68}N^4H^{35}O^{10},2HO$, which requires 68·34 p. c. C., 9·38 N., 6·20 H., 16·08 O. Its formation requires the presence of oxygen, and is represented by the equation—

$$C^{68}N^4H^{35}Fe^2O^{10} + 2HSO^4 + O^2 = C^{68}N^4H^{37}O^{12} + 2FeSO^4.$$

When on the other hand hæmatin is acted upon by sulphuric acid in closed vessels, *hæmatolin* $C^{68}N^4H^{39}O^7$ is formed, which is but very slightly soluble in sulphuric acid and very slightly soluble in caustic potash. Composition by analysis, 72·94 p. c. C., 10·02 N., 6·95 H., 10·09 O.; by calculation, 72·98 C., 10·02 N., 6·98 H., 10·02 O.

When hæmin crystals (p. 400) are heated with trichloride of phosphorus containing free phosphorus to 140° in closed tubes for six or eight hours, a purple-brown liquid is formed, which gives a spectrum with three absorption-bands, one between C and D close to C, a second between D and E nearer E, and a third between *b* and F, beginning from *b* and extending to the middle between *b* and F. No gas is evolved on opening the tube, but an easily separable crust forms on the sides. This substance is partly soluble in water, the solution giving the same spectrum as that of hæmatoporphyrin. From the part insoluble in water a substance is obtained resembling hæmatin; it contains phosphorus and gives by analysis, 52·67 p. c. C., 7·48 N., 5·11 H., 8·02 P., 26·72 O.: hence its formula appears to be $C^{68}N^4H^{39}P^4O^{26}$, or $C^{68}N^4H^{35}O^{10}.2PH^2O^8$ (calc. 52·78 C., 7·24 N., 5·05 H., 8·02 P., 26·91 O). The agreement of the spectrum of this substance with that of hæmatoporphyrin seems to show that the latter consists of $C^{68}N^4H^{35}O^{10}.2HO$, or that it is a hydrate of the same molecule as that contained in the phosphorus-compound (Hoppe-Seyler, *Med.-chem. Unters.* 1871, 523). ¶

5. Dry hæmatin introduced into *chlorine* gas takes up half its weight of chlorine, without giving off hydrochloric acid, and acquires a dark green colour; the resulting compound (containing 43·61 p. c. C., 3·40 H.) dissolves in alcohol, forming a neutral, bile-green precipitate which turns red when heated with hydrosulphate of ammonia, and straw-yellow when boiled with potash (Mulder). Hæmatin suspended in water is decolorised by a stream of chlorine, white flocks being separated, while ferric hydrochlorate remains in solution with only a small quantity of organic matter. (Lecanu; Mulder.) The flocks

heated to 100° give off chlorous acid and dry up to a non-ferruginous straw-yellow powder containing 36·87 p. c. C., 3·01 H., 5·89 N., 29·42 Cl.; this powder dissolves in oil of vitriol with evolution of gas and then blackens, dissolves in nitric acid without colour, in cold aqueous ammonia, in potash-ley with red colour, easily in alcohol and ether (Mulder). Solutions of hæmatin in alcohol containing sulphuric acid or ammonia become dark green when chlorine gas is passed through them, then yellowish bile-green, and finally colourless (Mulder).

6. Hæmatin heated with strong *alkalis*, or with a large quantity of *ammonia*, is converted into a body whose solutions are dark red in comparatively thick, dirty olive-green in thinner layers; it dissolves also with the same colour in alcohol containing sulphuric acid. These solutions do not yield any more crystals of hæmatin, and when mixed with hydrosulphate or stannite of ammonia, they do not exhibit the absorption-bands of reduced hæmatin. When hæmatin is evaporated to dryness with excess of ammonia, and the residue is dissolved in alcohol containing sulphuric acid, the resulting solution exhibits the spectrum of unaltered hæmatin, faint and diffuse, but not that of reduced hæmatin after addition of hydrosulphate of ammonia (Hoppe-Seyler). More recently Hoppe states that even boiling concentrated potash-ley is not capable of decomposing hæmatin.

When *phosphoretted hydrogen* is passed into ammoniacal hæmatin, the liquid becomes greenish, and the absorption-spectrum disappears, but is not replaced by that of reduced hæmatin. Acid solutions of hæmatin are likewise decomposed but more slowly (Koschlakoff & Popoff, *Chem. Centr.* 1867, 696).

Hæmin crystals dissolved in ammoniacal water, or a similar solution of hæmatin prepared by Wittich's method, exhibit, after addition of ferrous or stannous oxide, the two bands of reduced hæmatin, mostly very faint but not disappearing on agitation with air. The same two bands are exhibited by the ethereal solution which is obtained by shaking the ammoniacal liquid with glacial acetic acid and ether for 24 hours; afterwards the three bands of the normal hæmatin solution make their appearance. Alkaline hæmatin mixed with hydrosulphate of ammonia exhibits the same absorption-spectrum as hæmoglobin when similarly treated; ether does not take up anything from this solution after addition of acetic acid (Nawrocki, *Chem. Centr.* 1867, 690).

Combinations.—Hæmatin is insoluble in *water*.

Hydriodate of Hæmatin.—When the chloride of sodium to be used in the preparation of hæmin is replaced by iodide of potassium, iodated crystals are obtained resembling hæmin (Hoppe-Seyler).

Hydrochlorate of Hæmatin.—Strong hydrochloric acid, according to Lecanu, withdraws iron from hæmatin, and according to Mulder, does not dissolve it even on boiling. In hydrochloric acid gas, hæmatin assumes a reddish violet colour, takes up 6 to 13 p. c. hydrochloric acid, and then dissolves in alcohol (Mulder).

The *hæmin crystals*, first described in 1853 by Teichmann (*Zeitschr. f. rationelle Medicin.* neue Folge 3, 375), were recognized by Hoppe-Seyler as hydrochlorate of hæmatin.

Preparation. Defibrinated blood strained through linen is mixed with a large excess of solution of common salt, prepared by mixing 1 vol. of a saturated salt solution with 9 vol. water; the blood-corpuscles are left to settle down in the cold; the liquid is decanted; the pulp of blood-corpuscles shaken up with ether; the ethereal layer poured off; and the filtered aqueous solution dried at 50°. The pulverised and sifted residue is triturated with glacial acetic acid, and introduced into a flask with so much of the same acid that 2 litres of glacial acetic acid shall be present for every 100 gr. of the pulverised blood-corpuscles. The liquid is then warmed in the water-bath slowly and with agitation, kept for some hours at a temperature near 100°, and filtered, whereupon a mixture of hæmin crystals and tumefied albumin remains on the filter, and a solution runs off, which may be used for the preparation of fresh quantities of pulverised blood-corpuscles. The contents of the filter are suspended in water, and digested for some hours on the water-bath till the albuminous substances are dissolved; and the solution is left to itself for some days till the hæmin crystals have settled down, and then decanted. The crystals, washed by frequently pouring water upon them and decanting, are again digested for some hours with glacial acetic acid at 100°, collected after standing for some days in contact with the acetic acid, and washed with water, alcohol, and repeatedly with ether. To recrystallise them, they are triturated with dry carbonate of potash and alcohol, and left for a day; the liquid is filtered; the filtrate mixed with an equal volume of water and with glacial acetic acid; and the hæmatin which precipitates in flocks is collected, washed, and reconverted into hæmin, by digesting it, without previous desiccation, with pulverised common salt and excess of glacial acetic acid. The above is J. Gwosdew's method (*Wien. Acad. Ber.* 53, 683; *Jahresber.* 1866, 746) modified by Hoppe-Seyler—Gwosdew himself triturates dried defibrinated blood with $\frac{1}{5}$ pt. carbonate of potash; digests it at 40°—50° with alcohol of 93 p.c.; filters; dilutes; precipitates with acetic acid; dries the brown flocks at 100°; triturates them with $\frac{1}{5}$ pt. common salt and 20 to 30 pts. glacial acetic acid; and digests at 60°, whereupon the crystals separate out. Hoppe-Seyler did not obtain any hæmin crystals from dried hæmatin by treating it with common salt and glacial acetic acid. See also (*Tübinger medic.-chem. Unters.* 1, 297).

Or: blood or blood-corpuscles which have been immersed in salt-water, are coagulated by immersion in alcohol or boiling water; the coagulum collected on a filter is drenched, while still moist, with alcohol containing sulphuric acid; the liquid is warmed for a while; and the brown filtrate (Lecanu's hæmatin-solution) is mixed with saturated acetate and carbonate of soda till the solution exhibits only a faint acid reaction, and the hæmatin has separated, which separation may be accelerated by adding water and distilling off the alcohol. The brown precipitate collected and washed serves for the preparation of hæmin crystals (Hoppe-Seyler).

Hæmin forms violet-grey, metallically lustrous, glittering, very thin, rhombic crystalline plates, which appear brown by transmitted light, and make a coffee-coloured streak on porcelain. It does not alter at 200°; glows when more strongly heated in contact with the air, giving off a large quantity of prussic acid without intumescence, and leaving ferric oxide. Dissolves in oil of vitriol without evolution of gas, forming a violet-red liquid which gives off hydrochloric acid when heated. It is not attacked by nitric acid of sp. gr. 1·2 in the cold, but completely decomposed at 100°.—Does not dissolve in water either hot or cold; is nearly insoluble in strong hydrochloric acid and glacial acetic acid in the cold, but dissolves more abundantly when heated. Dissolves with decomposition in aqueous ammonia and caustic fixed alkalis, and the precipitate thrown down from these solutions by acids no longer yields crystals of hæmin with common salt and glacial acetic acid. Nearly insoluble in aqueous carbonate of soda, quite insoluble in alcohol and ether, but dissolves easily in alcohol which has stood over carbonate of potash (Hoppe-Seyler).

			Hoppe-Seyler. *at* 105° to 120°.		
		a.			*b.*
C	60·82	61·14	61·02	63·36	62·15
N	8·22				
H	5·51	5·40	5·57	5·45	5·57
Fe	8·40	8·47	8·73	8·63	8·77
Cl	3·96	4·83	3·47		3·78

b is recrystallised hæmin. Hoppe-Seyler regards all the products analysed, but especially the recrystallised hæmin, as mixtures of hæmatin free from hydrochloric acid and hydrochlorate of hæmatin. Thudichum (*J. pr. Chem.* 104, 281) doubts the existence of hydrochloric acid in the hæmin crystals.

As these crystals are obtained either from fresh or from boiled blood by treatment with glacial acetic acid, and from coagulated blood from which the salts have been washed out, after addition of common salt and glacial acetic acid, their formation may be made available for the detection of blood in forensic investigations. *Vid.* Brücke, (*Chem. Centr.* 1859, 212; *Jahresber.* 1857, 609); E. Scriba (*N. Jahrb. Pharm.* 11, 289; *Jahresber.* 1859, 707); Erdmann (*J. pr. Chem.* 85, 1); Wessel (*N. Br. Arch.* 118, 217); Blondlot (*Chem. Centr.* 1868, 750).

Hæmatin dissolves easily in water containing *ammonia*, *potash*, or *soda*, forming blood-red solutions, but does not neutralise these bases (Lecanu). Mulder's hæmatin is nearly insoluble in dilute ammonia-water, but dissolves in dilute carbonate of potash (Mulder). Ammoniacal hæmatin, evaporated over the water-bath, leaves an ammoniacal residue mostly soluble in water (Hoppe-Seyler). Hæmatin dissolved in aqueous alkalis is red in thick layers, olive-green in thinner layers (Hoppe-Seyler). Aqueous *borax* also dissolves hæmatin (Simon). Concentrated aqueous carbonate of potash precipitates hæmatin-solutions (v. Wittich). — From alkaline solution hæmatin is precipitated by acids in red-brown flocks, the liquid becoming colourless.

Ammoniacal hæmatin precipitates brown flocks from *hydrochlorate of baryta* and *hydrochlorate of lime.*

The solution of hæmatin in alkaline water, neutralised as completely as possible with acetic acid and filtered, forms a flocculent brown precipitate with the *neutral* and *basic acetates of lead;* grey-green with *cupric acetate;* grey-brown with *silver nitrate;* brown with *potassium ferrocyanide*, after addition of sulphuric acid, the supernatant liquid remaining green; it colours *potassium sulphocyanide* blood-red, and throws down flocks of the same colour (Simon).

Hæmatin is precipitated from its alkaline alcoholic solution by *lead acetate* as a grey-red mass, also by *cupric sulphate* (v. Wittich). When the solution in ammoniacal alcohol is mixed with *silver nitrate*, a dark brown precipitate is formed, containing 15·5 p. c. silver, whilst the liquid becomes colourless, and does not contain in solution any organic substance, or iron (Mulder).

An alkaline solution of hæmatin mixed with *cyanide of potassium* has a peculiar brown colour, and exhibits peculiar optical characters, but yields unaltered hæmatin when treated with acids (Hoppe-Seyler).

Hæmatin is insoluble in cold, somewhat soluble in boiling *alcohol*, easily in alcohol containing sulphuric, hydrochloric (Lecanu), nitric, arsenic, or acetic acid, or in alcohol on addition of carbonate of ammonia, fixed alkaline carbonates, borax, or acetate of soda (Simon). The alkaline alcoholic solution becomes green when boiled, but does not deposit anything (v. Wittich). It is insoluble in *ether*, *acetic ether*, *volatile oils*, *fied oils*, and *sulphide of carbon* (Lecanu; Simon). Dissolves with brown colour in *creosote* (Simon). Mulder's hæmatin dissolves in oil of turpentine, and in olive oil. — Dissolves slightly, with brown colour, in *glacial acetic acid*, especially on boiling (Hoppe-Seyler); the solution is precipitable by water (v. Wittich).

¶ *Hæmochromogen.* From the most recent experiments of Hoppe-Seyler (*Med.-chem. Unters.* 1871, 523), it appears that hæmatin is not a direct product of the splitting up of hæmoglobin, but results from such a decomposition accompanied by oxidation. This oxidation takes place, however, so rapidly, that it is only by special precautions that the non-oxidised products can be obtained. When, however, a solution of hæmoglobin is reduced by hydrogen and decomposed by alcohol containing sulphuric acid or caustic potash, in an apparatus from which oxygen is completely excluded, a colouring matter is produced, which is acid, has a purple-red colour in alkaline solutions, and is characterised by certain definite absorption-bands. It is this substance, *hæmochromogen*, which yields hæmatin by oxidation.

It has not yet been isolated, or regenerated by reduction of hæmatin, but its spectrum agrees generally with that of reduced hæmatin (p. 397). Hoppe-Seyler supposes it to have the composition $C^{34}N^2H^{18}FeO^5$, and represents the formation of hæmatin from it by the equation—

$$2C^{34}N^2H^{18}FeO^5 + 2O = C^{68}N^4H^{34}Fe^2O^{10},2HO. \quad ¶$$

Appendix to Hæmatin.

Blood-crystals of doubtful Nature. Hæmatoïdin. Erythrosin.

Crystals obtained by the following processes cannot be referred with certainty, either to hæmatin or to hæmoglobin, and are, perhaps, hydrochlorate of hæmatin.

a. When blood is kept at about 30° in contact with air which has been filtered or ignited, so that no putrefaction takes place, it becomes darker and filled with numerous brown and red blood-crystals, the corpuscles at the same time disappearing (Pasteur, *Compt. rend.* 56, 739).

b. R. Schwarz's *Hæmatin.*—When the clot of ox-blood, comminuted and freed from serum, is pressed; the liquid which runs off, shaken up in small portions with saturated aqueous oxalic acid, with addition of alcohol and a large quantity of ether; and the dark-brown liquid decanted after some minutes, then mixed with chloride of calcium and set aside for several weeks,—there are formed, together with oxalate of lime, small black druses consisting of cubes, which may be freed from lime by dilute hydrochloric acid.—Horse-blood thus treated yields, after partial evaporation and standing, small reed-like or spindle-shaped crystals, red-brown by transmitted light. On distilling off a third part of the ether, and mixing the remaining liquid with a large quantity of water, black-brown flocks are deposited, which may be purified by washing with water, boiling with concentrated acetic acid, again washing with water, alcohol, and ether, and, finally, with water. In this manner, also, the above-described crystals may be purified.

Scentless and tasteless, amorphous or crystalline mass, which, when burnt, leaves ferric oxide with small quantities of phosphate of lime.

Insoluble in oil of vitriol or concentrated hydrochloric acid, easily soluble in acidulated alcohol, also in weak alkaline or ammoniacal water, and precipitable from the latter solution by lead, copper, or silver salts. The solution in acidulated alcohol is decolorised by boiling with peroxide of lead.

Insoluble in water, cold alcohol, and ether, and precipitated by water from its solution in acidulated alcohol (R. Schwarz, *Zeitschr. f. gesammte Naturwissensch.* 11, 225; *Jahresber.* 1858, 561).

				R. Schwarz.	
			Amorphous.		*Crystals.*
46 C	276	66·34	64·12	63·89	64·03
3 N	42	10·10	10·19		10·17
22 H	22	5·26	5·31	5·28	5·66
Fe	28	6·73	6·36		
6 O	48	11·57	11·00		
$C^{46}N^3H^{22}FeO^6$	416	100·00	96·98		

Schwarz's amorphous hæmatin still retained 3·02 p. c. phosphate of lime. The crystals were obtained from horse-blood.

c. Rollet's *Hæmatin-crystals.*—Defibrinated blood is mixed, according to v. Wittich's method (p. 396), with very concentrated carbonate of potash; the liquid is filtered and evaporated; the dried residue exhausted with absolute alcohol; and the solution mixed with very dilute alcoholic tartaric acid till the red flocks at first precipitated have turned white.—The slightly acid liquid, filtered and evaporated at 65° to one-tenth of its bulk, yields, on cooling, large crystals which must be dried on paper and purified by boiling with water.—Brown crystals, black in the mass, and appearing under the microscope in flat prisms or tablets with rhombic or hexagonal outline. Double-refracting and pleochromatic, with a fine blue-green iridescence in reflected light. The crystals do not alter at 160°, and when burnt leave, without tumefaction, a quantity of ferric oxide corresponding to 7·31 p. c. iron. They are insoluble in water, either hot or cold, sparingly soluble in alcohol and ether, and dissolve easily and with brown-red colour in acid or alkaline alcohol, forming a dichromatic liquid, which is bottle-green in thin layers, garnet-red in thicker layers. With alkalis, oil of vitriol, nitric acid, and hydrochloric acid, they react like hydrochlorate of hæmatin (Rollet, *Wien. Acad. Ber.* 48, 223; *Chem. Centr.* 1864, 364; *Jahresber.* 1863, 644).

d. Virchow's *Hæmatoïdin.*—This substance frequently observed in decomposed blood and in old extravasations, occurs sometimes in the amorphous state in granules, spherules, and jagged masses, sometimes in well-defined monoclinic crystals having the form of obliquely truncated prisms not unlike those of gypsum, frequently also approaching to the rhombohedral form, often also in needles. They are strongly refractive and transparent, of yellow-red, red, or ruby-red colour, insoluble in water, alcohol, ether, acetic acid, and dilute mineral acids; the smaller crystals were often seen by Lehmann (*Lehrb. d. Physiol.* 1, 291) to be dissolved by alcohol containing sulphuric acid or ammonia, and precipitated on neutralisation. According to Virchow, concentrated alkalis and mineral acids do not act in the same manner on all specimens of hæmatoïdin; on addition of potash, the mass generally assumes a glowing red tint, gradually becomes porous, and splits up into red granules which gradually dissolve; the substance is not reprecipitated on neutralising the alkali.

Under the influence of strong mineral acids, especially of sulphuric acid, the sharp contours of the crystals disappear, and the colour of the roundish concretions gradually changes to brown-red, then to green, blue, and rose-colour, and finally degenerates into a dirty yellow. In the acid liquid produced by the decomposition of hæmatoïdin, iron may often be detected, often not.

Ch. Robin and Mercier (*Gaz. méd.* 1855, 44, 46, 48, 49; *Jahresber.* 1855, 738) found in a hydrated cyst of the liver, oblique prisms of hæmatoïdin with rhombic base (angles = 118° and 62°) and needles, insoluble in water, alcohol, ether, glycerin, volatile oils, and acetic acid, easily soluble in ammonia, less easily in potash or soda. Nitric acid also dissolved them quickly, hydrochloric acid less quickly, sulphuric acid not at all. When burnt, they gave off the smell of burning horn. They contained, according to two analyses, 0·0002 p. c. ash (no lime, traces of alkali-salts, and a considerable proportion of iron), and further consisted of 65·0 to 65·9 p.c. C., 6·4 to 6·5 H., 10·5 N., and 17·2 to 18·0 O., without sulphur or phosphorus. From these numbers Robin calculates the formula $C^{14}NH^{9}O^{3}$ (64·1 C., 6·9 H., 10·7 N.). Städeler proposes the formula $C^{30}N^{2}H^{18}O^{6}$ (calc. 65·7 C., 6·6 H., 10·2 N., 17·5 O.).

See further (*Handbuch.* viii., 140; *Lehmann's Physiological Chemistry,* i. 303; iii., 472).

Hæmatoïdin is regarded by Jaffé and others as identical with bilifulvin (p. 70), a view which is questioned by Städeler, on account of the reaction of hæmatoïdin with nitric acid observed by Robin.

The body described as hæmatoïdin by Holm (*infra*) is undoubtedly different from the colouring matters of bile, especially from bilirubin, but probably also from the hæmatoïdin of Virchow, Jaffé and Salkowski, inasmuch as it was obtained from *Corpus luteum.* It is here described as hæmolutein (p. 413). Hæmatoïdin from an apoplectic brain was observed by Holm to dissolve in chloroform with yellow colour, changing to light-green after exposure to light for a few days.

Salkowski (*Tübinger medic.-chem. Unters.* 1, 436) obtained from a strumous cyst, microscopic, well developed rhombic tablets, which dissolved sparingly in ether, easily and with golden-yellow colour, in chloroform. These solutions were decolorised by agitation with weak soda-ley, the colouring matter passing into the alkaline liquid. The alkaline solution gives with nitric acid a very transient blue colour, and becomes green on exposure to the air.

According to this, the body produced from decomposed blood-red exhibits the reactions of bilirubin. On the other hand, if the colouring matter of the ovary be regarded as a separate substance, namely, hæmolutein, the existence of hæmatoidin as a distinct colouring matter becomes doubtful.

Sanson (*J. Pharm.* 21, 420) obtained from ox-blood, besides the red colouring matter, a *yellow*, a *blue*, and a *brown* colouring matter. The the first of these is probably identical with Simon's *Hæmophein* (*N. Br. Arch.* 25, 51), a body which imparts a yellow or brown colour to serum and to fat prepared from blood. The blue colouring matter, Simon (*N. Br. Arch.* 29, 139) was unable to find; according to Gmelin, it proceeded from the filter-paper used.

The *ureters of the ox* contain a body which acquires a beautiful violet colour on exposure to the air. When the ureters freed from fat are triturated with pounded glass and exhausted with alcohol, the liquid evaporated and precipitated with neutral acetate, then with basic acetate of lead, and the filtrate with cupric acetate,—cuprous oxide and hypoxanthine are thrown down, and a dingy purple liquid is obtained, which is to be freed from metals by sulphuretted hydrogen, then filtered and concentrated. The colouring matter then separates as a violet film, which dissolves with yellow colour in dilute mineral acids and in hot dilute acetic acid, and is precipitated in violet flocks by ammonia. This colouring matter is insoluble in aqueous alkalis, alcohol, ether, sulphide of carbon, chloroform, and benzene (Holm, *J. pr. Chem.* 106, 150).

e. Städeler's *Erythrosin.*—By dissolving tyrosine in nitric acid and evaporating, there is obtained—besides colourless needles of nitrate of tyrosine—a red-brown residue, the formation of which is completed by repeated stirring with water and evaporation. This colouring matter resembles hæmatin or hæmatoïdin. After washing with water and drying, it is amorphous, dark red-brown, insoluble in the ordinary solvents, easily soluble in alcohol containing sulphuric acid, and partly precipitable from this solution by ammonia. The solution then remains coloured, appearing greenish by transmitted, red and opaque by reflected light. On evaporating the ammoniacal solution, the erythrosin remains as a dark brown substance, slightly soluble in water, insoluble in alcohol and ether, easily soluble in acidulated alcohol and in aqueous alkalis. The alkaline solutions are brown-red or dark violet, and become green when heated in contact with the air (Städeler, *Ann. Pharm.* 116, 87).

Colouring Matters of Urine.

1. The occurrence in normal and morbid urine, of an *indigo-forming substance*—indican according to Schunck (xvi, 1),—has been demonstrated by Schunck, Carter, and lately with certainty by Hoppe-Seyler (*Arch. pathol. Anat.* 27, 388). This substance imparts to urine the property of either depositing indigo, or of acquiring a violet or blue colour, when left at rest after being heated with nitric or hydrochloric acid.

As identical with this indigo-blue, or, at all events, as a product of the decomposition of indican, the following colouring matters of urine may be more or less confidently regarded.

a. The *Cyanurin* of Braconnot (*Ann. Chim. Phys.* 29, 252 ; *Schw.* 46, 340). It is a blue nitrogenous powder, which dissolves in dilute acids, even in organic acids, with brown-yellow to red colour, and is reprecipitated with blue colour by ammonia, lime-water, carbonate of lime, or carbonate of magnesia.—*b.* The *Cyanurin* of A. Spangenberg (*Schw.* 47, 487), which dissolves with blue colour in boiling alcohol and ether, and is reprecipitated by water.—*c.* The *blue urinary sediments*, observed by Simon (*J. pr. Chem.* 22, 120), Sammola (*J. Chim. méd.* 23, 419), Reinsch (*Jahrb. pr. Pharm.* 8, 93), Dumesnil (*N. Br. Arch.* 39, 48), Bouchardat (*N. J. Pharm.* 2, 539), and others.—*d. Urine-blue*, the *urocyanin* of Martin & Buchner (*N. Br. Arch.* 81, 62) which reacts in other respects like indigo-blue, but dissolves in boiling alcohol.—*e.* The *urocyanose* of Fordos, which crystallises in right prisms of a fine blue colour.

Respecting the detection of indican, according to Schunck and Carter, see xvi, 1.

Scherer (*Ann. Pharm.* 57, 180—195) and Heller (*Heller's Archiv.* 1845, 161—173) found, especially in Brightean urine, a highly carbonised pigment, which when dried had a coppery lustre like that of indigo, and dissolved in alcohol with splendid purple-blue colour.

Virchow (*Verh. d. physik.-med. Ges. zu. Würzburg*, ii. 303—308) who had formerly noticed Braconnot's cyanurin (*Arch. p. path. Anat.* i, 423), observed that the clear urine of a boy suffering from pains in the bladder and incontinence of urine, deposited, on exposure to the air, a flocculent sediment, which gradually turned blue, and then separated as a deposit consisting of slender radiate needles of an indigo-blue colour, mostly grouped in stars, and indifferent towards the strongest chemical reagents. It dissolved in strong alcohol, forming a deep-blue liquid. In a second case, Virchow found that the urine of a man suffering from very advanced granular atrophy of the kidneys, yielded, when boiled with hydrochloric acid (or with nitric, but not with acetic acid) a dark blue or violet sediment, resembling the former in every respect: continued boiling with the mineral acid appeared to destroy the colouring matter. The substance collected on a filter dissolved partially in ether, with violet-red colour, the remainder in absolute alcohol with fine blue colour. The entire substance gave, with alcohol, solutions whose colour sometimes inclined to blue, sometimes to reddish-violet or brownish. The crystals were not altered by alkalis; when treated with potash, under the microscope, they assumed a fine indigo-blue colour, and became somewhat more transparent, but otherwise resisted the action of the alkali. The sediment dissolved partially, with pale-yellowish colour, in ammonia, but the crystals remained undissolved as a brownish precipitate. But urine which yielded this pigment when heated with mineral acids, always passed into acid fermentation, attended with abundant formation of fungi, and assumed a deep yellow-brown colour when heated with potash and cupric sulphate. The blue crystals had the form of Heller's uroglaucin (*Hell. Arch.* 1845, Taf. I, figs. 4 and 5). Martin's urocyanin, which occurs especially in affections of the lungs and liver, is, according to Virchow, identical with Heller's uroglaucin. The statement of Heller that the urine in Bright's disease and in cholera is coloured blue on addition of a large quantity of strong nitric acid, has been confirmed by Lehmann (*Physiological Chemistry*, ii, 428), who, however, observed that this change of colour takes place only when uræmic symptoms have already set in.

Arthur Hill Hassall (*Phil. Mag.* September, 1853; *Chem. Gaz.* 1853, 335; 1854, 320) prepared from diabetic urine a blue substance "possessing all the characters of indigo." H. v. Scherer (*Ann. Pharm.* xc, 120—123) by mixing urine with a large quantity of mineral acid, whereupon the urine gradually assumed a darker colour, obtained a blue pigment, which, when washed and dried, formed a deep blue powder with copper-red streak, insoluble in cold and in boiling water, in dilute acids, and in alkalis, but soluble with blue colour in boiling alcohol, and more easily in ether.—The substance sublimes at 180°, for the most part undecomposed, in purple, shining, translucent prisms, which are insoluble in water, alcohol, and ether, and are undistinguishable from sublimed indigo. The substance is nitrogenous and rich in carbon; dissolves completely in strong sulphuric acid, with dark blue colour, like indigo. It is decomposed by chlorine, not bleached by sulphurous acid alone; forms a yellow solution with moderately strong nitric acid at the boiling heat. Ferrous oxide, sulphurous acid, sulphide of ammonium, &c., bleach the colouring matter in presence of alkalis or alkaline earths; atmospheric air or hydrochloric acid restores the colour of the substance in alkaline solution.

When normal urine is mixed with a small quantity of carbolate of ammonia, and then with nitric acid, it assumes a fine blue colour. The pigment thus formed exhibits the same reactions as one which occurs in the urine of cholera patients (see above), and is Parisel's *urocyanin* (Parisel, *Anal. Zeitschr.* 7, 398).

2. A *red, urinary pigment* is to be regarded, according to Schunck and Carter, as indirubin (xvi, 7). Fordos (*J. Pharm. Chim.* [4] 4, 163), who designates this red as *uro-erythric acid*, obtains it by mixing urine with half its volume of hydrochloric acid, setting the liquid aside for half an hour, and agitating with ether or chloroform. The red pigment dissolves more easily than the blue, in alcohol, chloroform, and benzene.

Harley (*Pharm. J. Trans.* xii, 243) evaporated urine to a syrupy consistence over the water-bath, continually removing the salts which separated, and added milk of lime to the boiling alcoholic extract of the residue till it was completely decolorised. The dried compound of lime and colouring matter was treated with hydrochloric acid and alcohol; the colouring matter was abstracted from the alcoholic solution by ether; and the ethereal solution freed as completely as possible from mineral substances and resin by water. The dry pigment (*uro-hæmatin*) forms a dark-red mass, which dissolves in alcohol and ether with splendid red colour, and contains iron. Iron was found, not only in the colouring matter of human urine, but also in that from the urine of oxen, horses, sheep, and pigs.

3. Attempts to isolate the normal pigment of urine have been made by Heller, Morin (*Ann. Chim. Phys.* 61, 13), Scherer, Harley, Schunck, and Thudichum.

Scherer (*Ann. Pharm.* 57, 180) precipitated fresh urine with nitrate of baryta; mixed the filtrate with neutral acetate of lead as long as a precipitate was formed; and treated the liquid filtered from this lead precipitate with basic acetate of lead. The finely pulverised precipitates were exhausted with warmed alcohol containing nitric acid, and the residue of the extract was lixiviated with water till the wash-water no longer gave any precipitate with nitrate of silver. The substance precipitated by neutral acetate of lead forms a powder of brownish to black colour, which dissolves sparingly in cold, more easily in warm water, easily in very dilute potash or carbonate of potash, or in water containing the salts of urine (common salt). In alcohol it dissolves with splendid purple-blue colour. Scherer found in it 54·43 p. c. carbon, 5·16 hydrogen, 8·43 nitrogen; the other pigment contains less carbon and more hydrogen.

Harley (*Verh. d. Physik.-med. Ges. zu Würzburg*, 5, 1) extracted from this urinary pigment by ether, a substance which imparted to the solvent a fine red colour, and proved to be identical with the urohæmatin above described; on evaporating the ethereal solution, crystals separated which had the form of margaric acid, but were soluble in alcohol, ether, water and ammonia. The solution has an acid reaction, due perhaps to hydrochloric acid still remaining.

Further, a mixture of Scherer's two pigments was completely exhausted with ether: the alcoholic extract of the residual pigment had a brownish-red colour and contained a ferruginous substance. The portion of the colouring matter not soluble in ether and alcohol yielded to water containing hydrochloric acid, a substance which coloured the solvent nearly black, and formed when dry, a black ferruginous powder, sparingly soluble in cold, more soluble in warm water. The fourth part of the pigment, insoluble even in dilute hydrochloric acid, yielded an ash containing silica and iron.

The ethereal and alcoholic extracts were then freed from the resin which adhered to the urohæmatin, by evaporating them nearly to dryness, and, after pouring off the still liquid portion, dissolving the residue in chloroform only so far as the colouring matter alone was thereby taken up. The solutions thus obtained had a very bright red colour. The dry preparation was insoluble in nitric, sulphuric, and hydrochloric acid, even at the highest degree of concentration, also in tartaric acid, oxalic acid, water, and solution of sodium or barium chloride, but soluble in caustic alkalis, alcohol, ether and chloroform; also in urine when warmed.

From the behaviour of urohæmatin to reagents and the presence of iron in it, Harley infers—as also Scherer concluded from the elementary analysis—that this urinary pigment is a modification of the hæmatin of blood. He supposes, however, that the urinary pigment is formed immediately from the pigment of bile and another pigment of the muscles.

Normal human urine behaves before the spectroscope like the pigment prepared from bile by dilute hydrochloric acid (p. 73), inasmuch as, in a layer 3 to 4 centim. thick, it exhibits an absorption-band at the limit of the green and blue. When urine is precipitated with basic acetate of lead, and the precipitate is decomposed by dilute sulphuric or oxalic acid, the reddish-yellow filtrate distinctly shows the γ-bands; soda-ley likewise produces in this solution the same alterations as in the acid solution of bile-pigment. These appearances are exhibited with peculiar distinctness by the deep red urine of fever patients; they are not altered by dilute mineral acids, by dilute alkalis, or by keeping the urine for weeks (Jaffé, *J. pr. Chem.* 104, 404).

Heller (*Heller's Archiv.* 1846, 21; *Pharm. Centr.* 1846, 597) distinguishes uroxanthin, uroglaucin, urrhodin and uroerythrin. *Uroxanthin* which is yellow, is present in normal, and more abundantly in morbid urine; it is decomposed by acids, with formation of a saccharine substance, uroglaucin and urrhodin, and is regarded by Neubauer (*Harnanalyse.* 5 Aufl. 37, Wiesbaden, 1867) as indican. — *Uroglaucin* and *urrhodin* are, according to Heller, oxidation-products of uroxanthin. Urrhodin remains, on evaporating the ethereal solution, as a solid amorphous mass, and on slowly concentrating the alcoholic solution, in nearly black indistinct crystals; it is carmine-red in very thin layers, insoluble in water, but dissolves with fine red colour in alcohol and ether.

Urinary concretions contain moreover yellow or yellow-brown *urophæin*, and hæmatin which produces a red-brown to black colour (Heller, *die Harnconcretionen*, Wien. 1860).

b. E. Schunck (*Proc. Roy. Soc.* 15, 1; *J. pr. Chem.* 97, 382; *Jahresber.* 1866, 750) distinguishes two normal urinary pigments or extractive matters, viz., *urian* $C^{86}NH^{51}O^{52}$, soluble in alcohol and ether, and *urianin*, $C^{38}NH^{27}O^{28}$, soluble in alcohol but not in ether. Both are very easily decomposible, and when heated in aqueous solution or subjected to the action of acids, take up water and become oxidised. Their formulæ are deduced from the analysis of the lead-compounds.

c. Thudichum (*Brit. Med. Journal*, N. S., 201, 509; *Schmidt's Jahrb.* 125, 154; *Neubauer* a. *Vogel's Harnanalyse*, 5 Aufl. 37, Wiesbaden, 1867; and further *J. pr. Chem.* 104, 257; abstr. *Chem. Centr.* 1869, 15) distinguishes a normal urinary pigment which he calls urochrome, and as decomposition-products thereof: uromelanin, uropittin and omicholic acid.

Urochrome. Urine is mixed with hydrate of baryta to alkaline reaction, for which purpose about 5 grms. of baryta-crystals are required to 1 litre of urine—then with a saturated solution of acetate of baryta; the liquid, after standing for 12 hours, is filtered; and the filtrate is precipitated with an ammoniacal solution of neutral acetate of lead. The lead precipitate is washed, and decomposed by trituration with dilute sulphuric acid; the liquid is filtered; the filtrate neutralised in the cold with carbonate of baryta, and again filtered; and the new filtrate is made alkaline by baryta-water and treated with carbonic acid. From the solution thus obtained, mercuric acetate throws down the colouring matter as a yellow precipitate, which is to be washed with cold and hot water, and decomposed by hydrosulphuric acid, whereupon the colouring matter immediately passes into solution, together with small quantities of hydrochloric and acetic acids. The hydrochloric acid is removed by moist oxide of silver—whereby, however, part of the urochrome is precipitated as a silver-compound, and acetate of silver is formed; the dissolved silver is removed by sulphuretted hydrogen; and the filtrate is evaporated over the water-bath (Thudichum).

Colourless amorphous yellow crusts, which partly dissolve in water, forming a yellow solution.

The aqueous solution when *kept*—more quickly in a warm atmosphere and in presence of acids—becomes darker, finally red, and deposits red flocks. No sugar is formed during this change. — Urochrome when exposed to the *air*, oxidises to a red body corresponding to uroerythrin. — When treated with *acids*, it forms three insoluble products which, by prolonged boiling of the acid solution of urochrome and mixing with water, are deposited in brown cohering lumps:— *a.* On treating these lumps with alcohol, *uromelanin* remains as a brown powder, soluble in caustic potash, precipitable by acetic acid. — *b.* The alcoholic solution has a fine red colour, is precipitable by water, and on treating the precipitate with ether, resinous *omicholic acid* is dissolved, while yellow *uropittin* remains behind. The latter separates from alcohol in crystals having the composition $C^{18}N^2H^{10}O^6$.

From aqueous urochrome, *neutral acetate of lead* throws down white flocks; the *basic acetate* yellow flocks; *mercuric nitrate* a white precipitate which becomes pale flesh-coloured on boiling. whilst the supernatant liquid turns red. *Mercuric acetate* throws down a yellow precipitate; *silver nitrate* a jelly soluble in nitric acid.

Urochrome dissolves in very dilute *mineral acids* and *alkalis.* It dissolves sparingly in *alcohol,* more freely in *ether.*

Uromelanin. — Obtained by decomposition of urochrome; also from the crude product formed from urochrome on exposure to the air. To obtain it directly from urine, the urine is mixed by drops with oil of vitriol, concentrated to one-half in a retort, and left to cool. From the precipitated resin, alcohol dissolves uropittin, while uromelanin remains behind.

Or normal human urine is left in a closed vessel for 12 months, then evaporated, whereupon it assumes a dark brown colour; the concentrated liquid is mixed with sulphuric acid, whereby uromelanin, uropittin, and omicholin are precipitated, together with a large quantity of benzoic acid; the precipitate is collected, and the benzoic acid dissolved out of it by boiling water; and the residue is freed by boiling alcohol from uropittin and omicholin, whereupon impure uromelanin remains in the form of a black powder. It is dissolved in very dilute potash-ley and filtered—which is possible only after deposition—then precipitated by dilute sulphuric acid, washed with water and with alcohol, and dried. It is pure if the preparation has been quickly conducted, but in the contrary case it contains uropittin which, after solution in the smallest possible quantity of ammonia and evaporation, may be dissolved out by water, the purer uromelanin then remaining undissolved.

Uromelanin forms a black, bulky, curdy precipitate, which dries up to a hard, brittle, shining, black mass.

Calculation, according to Thudichum.			Thudichum.	*mean.*
72 C	432	58·93	56·43 to 58·15	57·21
7 N	98	13·37	12·40 „ 13·38	12·88
43 H	43	5·88	4·28 „ 5·95	5·74
20 O	160	21·82		
$C^{72}N^{7}H^{43}O^{20}$	733	100·00		

Dissolves easily, but with decomposition, in *nitric acid*, forming a dark red solution. — Dissolves in fuming *oil of vitriol*, with purple red colour, and is precipitated therefrom by water. — Uromelanin suspended in water and treated with *chlorine gas*, becomes brownish, and after washing, dissolves in boiling alcohol, the solution on cooling depositing yellow-red amorphous flocks, which contain 47·2 p. c. C., and 4·4 H. — It is insoluble in water; dissolves very easily in *ammonia* and the *fixed alkalis*, and is precipitated by acids; there exists, however, a modification insoluble in alkalis. The ammoniacal solution is precipitated by the salts of the *earths* and of the heavy *metals*.

The *salts of uromelanin*, of which Thudichum has prepared the *barium*, *calcium*, *zinc*, *lead*, and *silver salts*, contain very variable quantities of metal; thus the barium salt contains from 7·2 to 13·75 p. c. Ba.; the silver salt 13·4 to 19·77 p. c. Ag. They are black, amorphous, sometimes gelatinous precipitates. — *Mercuric nitrate* added to the acetic acid solution, throws down a red precipitate. — Uromelanin is very sparingly soluble in *alcohol*, somewhat soluble in boiling *acetic acid*.

The *Alkaptone* of Dürr & Boedeker (*Ann. Pharm.* 117, 98; *Jahresber.* 1861, 806) was found in the urine of patients suffering from typhus and neuralgia. This urine, when mixed with caustic potash, became brown on exposure to the air, absorbed more than its own volume of oxygen, and even then reduced cupric oxide in alkaline solution.

To prepare it, the urine is precipitated with neutral acetate of lead, and after removal of this precipitate, with basic acetate of lead; the latter precipitate is decomposed under water by sulphuretted hydrogen; the filtrate containing hydrochloric acid is evaporated to a syrup, with addition of alcohol; and this residue is mixed with pulverised heavy spar, completely dried, pulverised, and exhausted with ether. The ether is evaporated; the crystals of hippuric acid which separate are removed, together with a small quantity of a dark-coloured powder insoluble in cold water; the solution is once more precipitated with neutral and basic acetate of lead; the precipitate decomposed with sulphuretted hydrogen; and the filtrate evaporated.

Yellow varnish, without taste or smell. Somewhat acid. Contains nitrogen, but no sulphur. — Melts when *heated*, burns with flame and a peculiar offensive odour. — With hot *nitric acid* it forms picric acid. — The solution mixed with aqueous *alkalis* or *alkaline earths*, acquires a brown-black colour on exposure to the air. Reduces *chromic acid* and *permanganic* acid; throws down cuprous oxide from excess of *cuprate of potash*, and metallic silver from *silver nitrate* when heated, or on addition of soda. — In a solution of *bismuth* it effects no reduction, even after addition of carbonate of soda. Not fermentable.—Dissolves in *water*. The solution is not altered by dilute *acids*. It is browned by *ferric chloride*, precipitated white by *basic lead acetate;* from solution of *mercuric nitrate* it throws down rust-brown flocks, from which on heating it reduces the metal.—Soluble in *alcohol*, nearly insoluble in *ether*.

In a brown urine from individuals suffering from melanotic carcinoma, there was formed, according to Hoppe-Seyler (*Arch. pathol. Anat.* 27, 388), besides indigo-blue, on exposure to the air a *brown colouring matter*, which was precipitable by basic acetate of lead, and could be dissolved out of the lead precipitate by carbonate of soda, or by alcohol containing sulphuric acid. When precipitated from the soda-solution by chloride of barium, and dissolved out of the precipitate by ammonia, it remained on evaporation as a shining, amorphous, very hygroscopic residue, still containing ammonia, easily soluble in water and in alcohol, precipitable by ammoniacal chloride of barium. This pigment contained neither nitrogen nor iron.

The *ferment of urine* is Béchamp's *Nephrozymase.* It imparts to normal human urine the power of converting starch into sugar. When filtered urine is precipitated with 2 or 3 vols. alcohol, and the separated flocks, containing the ferment, phosphates and albuminous substances, are washed with alcohol of 75 p. c., then with water, the aqueous solution thus obtained converts starch at 60°—70° into sugar, not however if it has been previously boiled. It does not alter cane-sugar; gives the reactions of the proteides with Millon's mercury-solution, and leaves on evaporation a residue, which burns with a smell of horn and leaves an alkaline ash (Béchamp, *Compt. rend.* 60, 45; *Anal. Zeitschr.* 4, 496).

Hæmolutein.

HOLM. *J. pr. Chem.* 100, 142; *Chem. Centr.* 1867, 712; *Kopp's Jahresb.* 1867, 779.
PICCOLO & LIEBEN. *Zeitschr. f. Chem.* [2], 4, 645.
THUDICHUM. *Centr. fur die medic. Wissenshaften*, 1869, 1; *Chem. Centr.* 1869, 65; *Deutsche chem. Gesellsch.* 2, 63.

Luteohæmatoïdin or Lutein. Ovariolutein.—Described by Holm (p. 405) as hæmatoïdin.—Occurs in the *Corpus luteum* of the ovary of the cow.

Hæmolutein occurs normally in yolk of egg, in the yellow bodies of the ovaries of other mammals, in blood-serum, in the cells of the fatty tissue, and in butter; abnormally in ovarian tumours, cysts, and serous effusions.—Also in the seed of maize, in the skins and pulp of berries, especially in annatto, in carrots, and generally diffused in the leaves, stamens, and petals of plants (Thudichum).

The identity of the colouring matter contained in these substances is shown by its behaviour before the spectroscope. The yellow solutions yield a spectrum distinguished by the brightness of its red, yellow, and green parts, and exhibiting three absorption-bands in the blue, indigo, and violet. The position of these bands varies slightly, according to the nature of the solvent (Thudichum).

Preparation. 1. The younger yellow and the older red bodies are cut out with the scissors, separated as completely as possible from the tissue, rubbed to a pulp with pounded glass, and then drenched with chloroform and left for several days. The deep golden-yellow solution leaves, on spontaneous evaporation, a viscid, yellow-red fat, which gradually solidifies to a crystalline mass, from separation of fat, cholesterin, and hæmolutein. This mass is resolved by agitation with absolute alcohol into a solution and a viscid portion, which latter encloses the hæmolutein, and from which the crystals of the latter may be isolated, though with some loss, by careful washing with ether (Holm). — 2. The *corpus luteum* is dried in the air, comminuted, and exhausted with ether; the ether is evaporated, and the residue boiled for eight hours with potash-ley, by which the fat is saponified. On mixing the resulting soap with water, the hæmolutein is deposited in small, very lustrous crystals, which may be separated by filtration (Piccolo & Lieben).

Properties. Separates from the solution containing fat, in microscopic, acute-angled, triangular tablets, one side of which is convex, or replaced by two straight sides. By aggregation of two or more of these crystals, rhombic tables or more complex forms are produced. By reflected light the crystals exhibit a fine cantharides-green colour, with metallic reflex: by transmitted light, they appear red, with fine blue and violet shadings; after washing with ether, they resemble recently prepared chromic acid (Holm). According to Piccolo & Lieben, the crystals of hæmolutein are red, or in a certain aspect, blue, and lose their colour in the air, especially if likewise exposed to light. According to Thudichum, hæmolutein forms yellow microscopic crystals, appearing orange or red when of a certain thickness.

Decompositions. *Oil of vitriol* colours hæmolutein blue, and dissolves it. — *Nitric acid containing nitrous acid* imparts to it a transient light-blue colour, changing to pale-yellow; the acetic acid solution is coloured blue, and afterwards decolorised, even by dilute nitric acid; the ethereal solution mixed with alcohol, and the chloroform solution, are not coloured by nitrous acid after addition of alcohol.

Combinations. Hæmolutein is insoluble in *water*, *aqueous ammonia*, *fixed alkalis*, and *mineral acids*, also in dilute *acetic acid*, but dissolves with golden-yellow colour in warm *glacial acetic acid* (Holm). According to Piccolo & Lieben, it is decomposed by boiling glacial acetic acid. — *Acetate of mercury* (mercurous or mercuric?) throws down hæmolutein completely as a yellow precipitate; *mercurous nitrate* separates it as a yellow precipitate, becoming white on boiling or standing.

Dissolves easily in *alcohol*, according to Thudichum; is insoluble according to Piccolo & Lieben, and Holm. Dissolves easily in *bisulphide of carbon* with flame-red colour, becoming orange-red when much diluted; easily, with golden-yellow colour, in *chloroform*, the solution not being altered by agitation with ammonia (Holm). Dissolves in *ether* somewhat less abundantly than in chloroform (Holm), and in *benzene* (Piccolo & Lieben), with yellow colour.

The colouring matter of egg-yolk consists, according to Chevreul and others, of a red portion corresponding to blood-red, and a yellow portion, corresponding to bile-brown. — According to Gobley, when egg-oil is heated with alcohol and left to cool, the yellow separates, together with olein and cholesterin, whilst the red remains in the mother-liquor. The *red* liquid, when frequently evaporated and redissolved, becomes darker, and after prolonged heating in the water-bath, deposits black granules which leave ferruginous ash when burnt. The yellow colouring matter does not form a green solution when treated for 24 hours either with hydrochloric acid or with alcohol and sulphuric acid; with dilute potash-ley, under certain circumstances, it becomes green (Gobley, *N. J. Pharm.* 9, 170).

The colouring matter of egg-yolk is hæmolutein, or a very similar body. When the non-coagulated yolk of hens' eggs is agitated with ether, colouring matter and fat are dissolved, and remain on evaporation as a yellow mass, changing to dingy-green when stirred up with nitric acid containing nitrous acid, — also with a small quantity of oil of vitriol, whereas a larger quantity of oil of vitriol colours it dirty-brown to brown-red.

When egg-oil, after exhaustion with ether, is saponified with soda-ley of 5 p. c. — whereupon an odour of train-oil is evolved, — the soap extracted with ether, and the ether evaporated, there remains a deep gold-yellow mass, which is non-saponifiable, or saponifies only with difficulty, and on standing gradually yields crystals of cholesterin together with deep red non-crystalline particles. It assumes a transient pure blue colour when triturated with strong nitric acid; dissolves in ether and chloroform with golden-yellow, and in bisulphide of carbon with orange colour; the colouring matter is not extracted from the solution by ammonia. The solution mixed with alcohol is decolorised by nitric acid containing nitrous acid, without exhibiting any previous play of colours (Städeler, *J. pr. Chem.* 100, 148; *Chem. Centr.* 1867, 715).

The colouring matter of the shells of birds' eggs is free from iron, and is first imparted to the eggs in the cloaca, not in the oviduct. The green or bluish colour of the egg-shells of *Sylvia phœnicurus*, *Turdus musicus*, *Corvus coroni*, and *Vanellus cristatus*, exhibits, after isolation by hydrochloric acid, the reactions of biliverdin (p. 77). The brown-red egg-shells of *Falco tinnunculus* and *Buteo vulgaris*, and the red spots of the eggs of many small singing birds contain cholepyrrhin (p. 71), traces of which are also found in eggs not coloured either green or brown, but not in the pale-yellow eggs of Cochin-China fowls (W. Wicke, *Götting. Nachr.* 1858, 314; *Kopp's Jahresb.* 1859, 642).

Pyocyanin.

FORDOS. *Compt. rend.* 51, 215; *N. J. Pharm.* 38, 165; *Chem. Centr.* 1860, 772; *Kopp's Jahresb.* 1860, 597. — *Compt. rend.* 56, 1128; *Chem. Centr.* 1863, 964; *Kopp's Jahresb.* 1863, 657.

LÜCKE. *Arch. f. klin. Chirurgie* 3, 135; *Chem. Centr.* 1863, 966; *Jahresb.* 1863, 658.

Formed occasionally in pus from wounds, which then colours the bandages blue. According to Lucke, its formation is connected with the presence of vibrios. See also Chalvet (*N. J. Pharm.* 38, 377). — The occurrence of a blue substance in pus had already been observed by Braconnot (*J. Chim. méd.* [3], 18, 454), Overbeck (*N. Br. Arch.* 81, 159), and Delore (*Compt.

rend. 51, 296), this substance being designated by Overbeck as *pyoverdin*, by Delore as *cyopyin*. In other cases the blue colour of pus is produced by ferrous phosphate (S. Schiff, *Ann. Pharm.* 106, 108; *Jahresb.* 1859, 192; Schlossberger, *N. Jahrb. Pharm.* 10, 81). On the pyin of Güterbock (see *Handbuch* viii, 526; *Lehmann's Physiological Chemistry* iii, 156). This substance is, according to Eichwald (*Wurzburg med. Zeitschrift.* 5, 298), a mixture of peptone with unaltered or modified mucin.

Preparation. The bandages are steeped in water; the pyocyanin and pyoxanthose are dissolved out of the extract by agitation with chloroform; and the pyocyanin is transferred to water by agitation with weak aqueous hydrochloric acid, the pyoxanthose then remaining digested in the chloroform. By mixing the aqueous solution with carbonate of baryta, filtering, agitating the filtrate with chloroform, and leaving the chloroform solution to evaporate, the pyocyanin is obtained in the separate state, and may be freed from adhering pyoxanthose by washing with ether (Fordos). Lucke proceeds in a similar manner.

Properties. Blue prisms or needles grouped in crosses or rosettes; according to Lücke, sometimes also blue or green laminæ. Melts when heated, and does not sublime.

The crystals of pyocyanin, as well as its solution in chloroform, become greenish-yellow on keeping, from formation of pyoxanthose. On washing the crystals with ether, the pyoxanthose dissolves, and the blue colour is restored (Fordos). Impure solutions become decolorised when left in closed vessels or heated with sulphide of sodium, and turn blue again (though not always, according to Lucke) on exposure to the air. — The aqueous solution is decolorised by chlorine, transiently also by carbonic acid, permanently by oil of turpentine (Lücke).

Pyocyanin is soluble in *water*. It unites with *acids*, which redden the aqueous solution; with *hydrochloric acid* it forms red four-sided prisms; with *acetic acid*, a red solution which loses acid on evaporation (Fordos). Strong acids decompose it when heated (Lücke). Alkalis turn the acid solution blue again (Fordos). The alcoholic or aqueous-alkaline solution is not precipitated by alum or by neutral acetate of lead (Lücke).

Pyocyanin dissolves in *alcohol* and in *chloroform*, less easily in *ether*.

Pyoxanthose. This yellow colouring matter of blue pus is obtained by evaporating the above solution in chloroform after addition of water, filtering the aqueous solution, extracting with chloroform, and evaporating. It then sometimes, though rarely, remains crystallised, forming confused groups of microscopic needles, slightly soluble in water, easily in alcohol, ether, chloroform, bisulphide of carbon, and benzene. It is reddened by acids, coloured violet by ammonia or potash (Fordos).

Chlororhodic acid. An acid sometimes occurring, according to Boedecker, in pus. Dried and pulverised pus is freed from fat by ether and boiled with alcohol of 75 p. c.; the liquid is filtered and evaporated, and the residue is boiled with water. The unfiltrable solution is freed by acetate of lead from substances precipitable by that reagent, then from excess of lead by sulphuretted hydrogen and evaporated. The chlororhodic acid is extracted from the residue by absolute alcohol, together with a little common salt, and remains on evaporation as a yellowish mass. — Loose chalk-white powder made up of small [illegible]; melts when heated, and burns with an animal odour.

The dry acid does not dissolve in boiling water till after addition of alkalis; this solution is not precipitated by acids, nor after neutralisation, by metallic salts, excepting stannous chloride, mercuric chloride, and mercuric nitrate, which throw down white flocks. Tincture of galls likewise throws down white flocks, tincture of iodine yellow flocks; chlorine-water colours the liquid a fine rose-red, the colour being destroyed, however, by excess of the reagent. The acid dissolves easily in alcohol, but is insoluble in ether (Boedecker, *Zeitschr. f. ration. Medicin:* rene Folge, 6, 198).

On the Chemical Composition of Pus, see Miescher, *Med-chem. Unters.* 1871, 441; *Chem. Soc. J.* [2] 9. — Hoppe-Seyler, *Med-chem. Unters.* 1871, 486; *Chem. Soc. J.* [2] 9; also ADDENDA to this volume.

Melanin.

L. GMELIN. *Schw.* 10, 507; *Handb.* 3, Aufl. 2, 1170.
SCHERER. *Ann. Pharm.* 40, 63.

L. Gmelin's *Black Pigment of the Eye* (*Augenschwarz*). Occurs as a thick coating on the choroid of the eye.

The carefully prepared choroïds of ox-eyes are cleansed from blood by immersion in water; the melanin is separated from the choroid with a camel-hair brush, then left to deposit, stirred up with water, and filtered through linen to remove residues of membranes; the liquid which runs through is evaporated; and the residue is boiled.

Brown-black lumps, dull, easily pulverised, sinking in water, infusible (Gmelin). — After deduction of 9·8 p. c. ash, it contains, on the average, 56·88 p. c. C., 5·95 H., 13·76 N., and 23·41 O. (Scherer). In the black pigment of goats' eyes, Schwarzenbach (*Pharm. Viertelj.* 11, 37) found 92·06 p.c. ferruginous inorganic constituents to 7·94 p.c. organic.

By *dry distillation* it yields, without tumefaction, empyreumatic products and carbonate of ammonia; the ash contains common salt, phosphate of lime, and ferric oxide. — Smoulders when set on fire. — *Chlorine-water* renders the colour of melanin paler, and half dissolves it; the undissolved portion is turned brown by aqueous potash; dissolves, and is precipitated in brown flocks by acids. — *Fuming nitric acid* dissolves it, with effervescence, to a red-brown, not bitter liquid, from which potash-ley and water throw down yellow-brown flocks. — *Oil of vitriol* dissolves it at a gentle heat, with evolution of sulphurous acid, forming a black liquid precipitable by water. — In hot aqueous *potash ley* it dissolves slowly and imperfectly, with evolution of ammonia, forming a red-brown liquid, from which hydrochloric acid throws down brown flocks soluble in cold potash. *Ammonia* acts less strongly than potash (Gmelin).

Insoluble in *water*, *dilute acids*, *lime-water*, *alcohol*, *ether*, and *oils*, both *fixed* and *volatile* (Gmelin).

A black pigment deposited in a diseased lung was found by C. Schmidt. (*Lehmann's Lehrbuch. d. physiol. Chemie*, 1, 296) to contain in two cases: *a.* 72·95 p. c. carbon, 3·89 nitrogen, 4·75 hydrogen, and 18·41 oxygen. — *b.* 66·76 carbon, 8·29 nitrogen, 7·33 hydrogen, and

17·61 oxygen. In other cases the black lung-pigment has been found to consist of carbon, or even of sulphide of iron (Perls, *J. pr. Chem.* 105, 81).

The black colouring matter found in the liver of patients suffering from melanotic cancer, consists of uromelanin (p. 411) (Thudichum). When the black nodules separated from the liver are left under water for a year, the putrefaction which ensues destroys the foreign substances, but not the uromelanin. (The further treatment as described in the *Chem. Centr*, is unintelligible, Kr). — Hard, amorphous, dark brown powder, without taste or smell. When heated it smoulders slowly, and without fusion, and burns away with an odour of horn. Dissolves easily in fuming nitric acid, forming a deep red liquid. Strong hydrochloric acid acts in a similar manner, whereas oil of vitriol scarcely acts upon it. Chlorine decolorises the melanin quickly in alkaline solution, slowly when suspended in acids. By fusion with potash, volatile fatty acids are produced.

Melanin swells up in water like albumin, and colours warm water brown. Dissolves in the aqueous hydrates, monocarbonates, and bicarbonates of the alkalis, also in aqueous urea, with evolution of ammonia if heat is applied. The alkaline solutions are precipitated by acids and salts; the solution in potash-ley becomes decolorised after standing for a year, and then yields a white precipitate with acids. Dissolves in boiling alcohol, with brown colour, not in alcohol containing sulphuric acid; insoluble also in chloroform and bisulphide of carbon.

After deduction of 1·47 p. c. ash, it contains on the average 51·73 p. c. carbon, 5·07 hydrogen, 13·24 nitrogen, and 29·96 oxygen, agreeing with the formula $C^{18}N^{2}H^{10}O^{8}$ (Dressler, *Prager Vierteljahrsschr. f. prakt. Heilkunde*, 88, 9; *Chem. Centr* 1866, 395).

According to Pribram (*Prag. Vierteljahrsschr. loc. cit.; Chem. Centr.* 1866, 397) a black pigment from the urine of a patient suffering from melanotic cancer of the eye, belongs to this place.

Sepia Black. — Examined by L. Gmelin (*Schw.* 10, 533); by Prout (*Thoms. Ann.* 5, 419) after exhaustion with water and hydrochloric acid.

Prout found sepia-ink to be infusible and difficult to burn; the ash contained a large quantity of ferric oxide. It was insoluble in warm hydrochloric and sulphuric acid; dissolved in nitric acid with red brown colour and evolution of nitrous gas; partly in warm aqueous ammonia, and in boiling potash-ley, forming a dark brown solution, from which it was partially precipitated by hydrochloric or sulphuric acid, not by nitric acid. — Gmelin found a small quantity of iron in the ash; the ink dissolved in oil of vitriol, and was precipitated by water.

Bizio (*Schw.* 45, 128) described as *Melam* the black of sepia, apparently altered by nitric acid, which he obtained by diluting sepia-ink with water, boiling the portion which remained on the filter with water and alcohol, then with dilute nitric acid (whereupon carbonic acid and nitric oxide were evolved), and washing out the adhering acid with aqueous carbonate of potash and with water. It is a soft black powder, which detonates when heated; is not decolorised by chlorine; is decomposed by strong nitric acid; and when heated with oil of vitriol, is converted, with evolution of sulphurous acid, into a pulpy mass, from which water separates unaltered melam. It dissolves completely in boiling water, forming a black solution, from which it is precipitated by mineral acids, metallic salts, and alcohol, scarcely at all in hot hydrochloric acid, in aqueous alkalis, even in the cold, and is completely precipitated from the black viscid solution by acids. Acetic acid, alcohol and ether do not dissolve melain.

The dried contents of the ink-bag of the cuttle-fish is, according to Hosæus, very hard and black; has a conchoidal fracture; sp. gr. 1·275; appears amorphous, even under the microscope; and contains, to 21 p. c. water, 11·02 p. c. ash, free from iron and phosphorus. The organic substance, after deduction of ash, contains 42·2 p. c. C., 9·9 N., 3·3 H., and 42·6 O. — The black is charred by oil of vitriol, and dissolved by nitric acid, mostly with red colour; hydrochloric acid dissolves the inorganic, and attacks the organic substance. Strong potash-ley dissolves the black, with fishy odour, forming a brown liquid; water, acetic acid, alcohol, chloroform, ether, and benzol do not dissolve it. — A fossil sepia from the Lias slate contained 36·8 p. c. ash; the black, less easily attacked colouring matter contained 63·8 p.c. C., 3·4 N., 7·2 H., and 25·6 O. (Hosæus, *N. Br. Arch.* 120, 27; *Chem. Centr.* 1865, 164; *Kopp's Jahresb.* 1864, 675). A sepia examined by Schwarzenbach (*Pharm. Viertelj.* 11, 37; *Kopp's Jahresb.* 1862, 539) contained to 80·63 p. c. colouring matter, 4·6 mucus, and 14·77 ash, likewise free from iron. It gave off ammonia without melting when heated; did not dissolve in aqueous ammonia, and was slowly decolorised by chloride of lime.

Colouring Matter in the Mantle of the Black Dew Snail. — The snails freed from their entrails are digested with moderately dilute nitric acid, till they assume a dirty flesh-colour; the violet solution is filtered; and the filtrate is treated with ammonia, which throws down a dark brown precipitate. — Black brittle mass, having the appearance of Indian ink, and still containing a large quantity of phosphate of lime. Insoluble in *water*. Dissolves in *mineral acids*, imparting to them a splendid violet to black colour. The solution in nitric acid becomes crimson after long standing, and is finally decolorised. — Insoluble in *alcohol*, very slightly soluble in *glacial acetic acid*, insoluble in *oils* either *fixed* or *volatile* (A. Vogel, jun., & Reischauer, *N. Repert.* 6, 355; *N. Jahrb. Pharm.* 9, 179; *Kopp's Jahresb.* 1858, 576).

Colouring Matters of Birds' Feathers. — The colours of birds' feathers are not always due to isolable pigments, but sometimes to optical phenomena. From those feathers which exhibit the same colour by reflected and transmitted light, colouring matters may be extracted, and among these the yellow, red, lilac, and green (*zoofulvin, zooerythrin, zooverdin*), are soluble in ether and alcohol, whereas the black *zoomelanin* is insoluble in these liquids, but soluble in ammonia and in potash The latter is probably identical with the melanin of the eye.

The red of the feathers of *Calurus auriceps* may be extracted with boiling alcohol, and remains, on evaporating the tincture at 60°—70°, as a dark, orange-coloured powder, which is altered by light, and dissolves in boiling water. From the light violet feathers of *Catinga cærulea*, boiling alcohol and acetic acid extract the colour; the latter solution becomes colourless on standing.

The beautiful blue-violet wing-feathers of the *Touracos* lose their colour when the bird gets wet, and then give a red stain. On drying, they recover their original colour, or acquire a blue colour if the bird has died in the interval. In the dead bird the colouring matter has become insoluble in water. When the feathers are soaked in ammonia-water, and the filtrate is precipitated with acetic acid, the pigment is obtained as a red powder (Bogdanow).

The pigment is Church's *turacin.* The beard of the feather is washed with alcohol and ether, and the colouring matter is extracted with water containing $\frac{1}{500}$ of alkali, and precipitated with hydrochloric acid.—Amorphous laminæ of deep violet-purple colour, crimson by transmitted light. Not altered at 100°, but above that temperature it becomes bluish dark green, begins to melt, and gives out violet fumes. Contains nitrogen and 5·75 to 5·89 p. c. copper, which cannot be removed by dilute acids. The solution exhibits a spectrum with two black absorption bands.—Dissolves with decomposition in fuming nitric acid, forming a deep brown liquid, and is decomposed by oil of vitriol. Dissolves in pure water, with rose-red colour, not in acid or saline water. Dissolves with blue colour in alkaline liquids; with concentrated alkalis decomposition takes place, and an odour of volatile bases is emitted. Insoluble in alcohol and in ether (Church, *Chem. News*, 19, 265; *Zeitschr. f. Chem.* [2], 5, 445).

Yellow-green feathers give up their colouring matter to hot acetic acid; after evaporation of the acid, the pigment dissolves in alcohol. The yellow pigment of the feathers of *Oriolus galbula* likewise dissolves in acetic acid, but the solution quickly loses its colour (Bogdanow, *Compt. rend.* 45, 688; 46, 780; 54, 660); the last paper also contains observations by Schlegel and J. Verreaux.

Colouring Matter of Crabs and Lobsters.—Occurs, according to Macaire, in two membranes situated beneath the calcareous shell; in the external green membrane and the calcareous shell itself it is found in the brownish-green state, from which it passes into red by heating to 62°—75° in the air or in oxygen gas (not in hydrogen or carbonic acid), or by putrefaction, or by the action of acids, alkalis, or salts; in the inner reddish membrane it exists already in the reddened state.—In crabs having very soft membranous shells, a blue pigment is deposited below, and a brownish-green pigment above the membrane which extends between the shell and the flesh (Witting).

The blue colouring matter of the river crab is nearly insoluble in water, but dissolves in alcohol with bluish colour, changing to red; it is coloured a fine crimson-red by ammonia, brick-red by acetic acid, and is apparently but little altered by chlorine. The pigment reddened by ammonia is not altered by hydrochloric acid. Carbonate of soda produces but little alteration in the pigment reddened by boiling water; it colours the unaltered pigment a fine purple-red, which colour disappears almost wholly on addition of hydrochloric acid, completely on addition of nitric acid. Crab shells also quickly become red on exposure to the air (Witting, *J. pr. Chem.* 73, 121; *Kopp's Jahresber.* 1858, 563).

By boiling crab skins with alcohol and evaporating, a fatty red fusible mass is obtained, which when heated, burns with evolution of ammonia and leaves a ferruginous ash. The red substance is decomposed by chlorine, nitric acid, or oil of vitriol, turned green in alcoholic solution by acids, and not restored by alkalis (Macaire). According to Lassaigne, it dissolves easily, with red colour, in dilute sulphuric acid, and according to Macaire, with the same colour in warm aqueous potash, whence it is precipitated by acids without alteration. The alcoholic solution is slowly decolorised by alum, and precipitated red on addition of ammonia. Neutral acetate of lead produces a copious violet precipitate. Crab-red dissolves with reddish-yellow colour in alcohol and ether, also in warm volatile oils, but not in fixed oils (Macaire, *Bibl. univ.* 1821; abstr. *Schw.* 33, 257; Lassaigne, *J. Pharm.* 6, 174).

The eggs of crabs and lobsters contain a colouring matter dissolved in albumin, identical with that which gives rise to the reddening of the shells on boiling. Lobster eggs yield when crushed a green albuminous liquid, which deposits the colouring matter on dilution with water. This colouring matter is green, resinous, and uncrystallisable, turns red when dried, even at ordinary temperatures, also in contact with dehydrating salts, alcohol, ether, and acids, and even when merely rubbed with a solid body. When the albuminous liquid of the eggs is heated, the albumin, as it coagulates, takes up the colouring matter, and is coloured red thereby. From this precipitate it is extracted by alcohol (Valenciennes & Frémy, *N. Ann. Chim.* 50, 165; *Jahresb.* 1854, 687).

According to Grote (*Compt. rend.* 1814, 44), when pulverised and boiled crab shells are heated with potash-ley till the liquid becomes orange-yellow, and the filtrate is mixed with hydrochloric acid and again heated, crab-red separates after a while in dark red flocks soluble in alcohol.

According to Göbel (*Schw.* 39, 426), the red pigment of the red feet and beaks of birds is identical with crab-red. On removing the epidermis from pigeons' feet after maceration in water, the pigment comes to light, and may be scraped off. After being dissolved in alcohol or ether, and recovered by evaporation, it appears red, of the consistence of tallow, melts in hot water to red oily drops which solidify on cooling, and makes permanent grease-spots on paper. It is decomposed by nitric and by sulphuric acid, is insoluble in water and acetic acid, but dissolves in potash-ley, from which it is precipitated by acids, and with fine red colour in alcohol, ether, and volatile oils. The colouring matter of crabs contains 68·18 p. c. C., 9·24 H., and 22·58 O.; that of the feet of pigeons and geese is similarly composed. All these pigments are free from nitrogen (Gobel).

Colouring Matter of the Purple-fish.—From *Murex brandaris* and *M. trunculus.* The fresh secretion is colourless, and on exposure to daylight turns first yellow, then green, blue, red, and finally purple; this change of colours takes place with *Murex brandaris* in two days, with *M. trunculus* in a few minutes.

The thoroughly dried secretion is opaque and black, but yields by trituration a deep red powder. It smells at first like *asafœtida*, and contains copper. Chlorine destroys the colour; strong nitric acid gives off nitrous gas and colours it golden yellow. Oil of vitriol destroys foreign admixtures without attacking the colour itself.—Insoluble in water and in dilute acids, even on boiling; insoluble also in cold aqueous ammonia, potash, and soda. Boiling potash-ley colours it yellowish, and deposits green flocks containing some of the undecomposed purple pigment (Bizio, *J. Chim. med.* 10, 99).

The colouring matter secreted by the sea-owl or lump fish, *Aplysia depilans*, a gasteropod occurring on the coasts of the Mediterranean, is a concentrated solution of aniline-red and aniline-voilet. It decomposes very easily in the dissolved state; if it be precipitated by sulphuric acid, and again from alcoholic solution by common salt, a substance is obtained which exhibits the reactions of aniline-violet. The colouring matter which remains dissolved after the precipitation by common salt may be separated by tannic acid, and like fuchsine, is decolorised by ammonia, and coloured red again by acetic acid (Ziegler, *Mult. Soc. Bull*, 37, 293; *Kopp's Jahresber.* 1867, 821).

On the purple pigment which sometimes makes its appearance on mouldy articles of food (bread, potatoes, meat), see Sette (*Schw.* 50, 415); Meylink (*Repert.* 43, 13), Buchner (*Repert.* 43, 88); Pelouze (*J. Chim. med.* 19, 586; *N. Ann. Chim. Phys.* 9, 5); Ehrenberg (*J. Chim. méd.* Oct. 1849); Oberdörffer (*N. Br. Arch.* 49, 43); Hubner (*N. Br. Arch.* 50, 302). According to Erdmann (*J. pr. Chem.* 99, 385; *Jahresb.* 1866, 670), this colouring matter exhibits the reactions of the aniline dyes, the red that of the salts of rosaniline, and a blue sometimes observed at the same time, that of the salts of triphenylrosaniline.

On the green colouring of oysters, see Valenciennes (*J. Pharm.* 27, 155); on the colouring matters of sweat: Schottin (*Pharm. Viertelj.* 2, 54); Landerer (*Repert.* 55, 234; *Handbuch*, viii, 302).

Proteides of the Vegetable Kingdom.

The nitrogenous and sulphuretted substances occurring in the vegetable kingdom, and formerly designated as *vegeto-animal substance*, have more recently been further distinguished according to the following considerations.

a. When the dough of wheat-flour is kneaded with water as long as the water becomes milky from separation of starch, there remains a grey elastic glutinous mass, the *gluten* of Beccaria (*Common. Bonon.* 1, 1, 122).

b. The expressed juice of many plants coagulates when heated, by separation of a similar substance (Rouelle, *Crell. Beiträge zu den chem. Ann.* 1, 3, 87); the substance thus separated resembles animal albumin: *Vegetable albumin* (Fourcroy, *Ann. Chim.* 3, 252), and gluten (Proust, *J. Phys.* 54, 199; *A. Gehl*, 5, 596).

c. Rye-flour yields coagulated *vegetable albumin* and *gluten* soluble in alcohol. When the flour is separated by stirring it up with cold water and leaving it to settle into sedimentary flour and a solution, the latter deposits the albumin on boiling, and from the filtrate concentrated to the consistence of honey, the gluten may be extracted by alcohol.—The same gluten is obtained when the sedimentary flour is separated by levigation into starch and a grey substance, and the latter is exhausted with alcohol (Einhof, *A. Gehl.* 5, 131); also Gunsberg (*J. pr. Chem.* 85, 214).

d. The wheat-gluten of Beccaria may be resolved, by treatment with alcohol, into residual *zymome* and soluble *gliadin*, which latter is obtained by evaporating the solution to the consistence of honey (Taddei, *Schw.* 29, 514).

According to this, the insoluble substance (obtained according to *c* or *d*) is to be distinguished from soluble *vegetable gelatin* (Berzelius).

e. Vegetable gelatin from gluten is accompanied by a *mucous substance*, which is obtained by macerating the vegetable gelatin in acetic acid, mixing with alcohol, and filtering, and remains on the filter in the form of a transparent gum (Berzelius, *Lehrb.* 3 Aufl. 6, 453). According to Berzelius, this substance is identical with Saussure's *mucin*, which is obtained by boiling gluten with alcohol, mixing the hot filtered decoction with an equal quantity of alcohol, concentrating to $\frac{1}{16}$, filtering from *gluten*, and evaporating the filtrate.

f. Leguminous fruits contain vegetable albumin and a substance different from vegetable gelatin, but likewise soluble in alcohol, which remains suspended in the water after the deposition of the starch, but is deposited on further dilution (Einhof, *A. Gehl.* 6, 126 and 548). This nitrogenous and sulphuretted constituent of leguminous fruits, obtained from the aqueous extract of peas by evaporation, or by precipitation with nitric acid, but in that case insoluble in alcohol, is the *Legumin* of Braconnot (*Ann. Chim. Phys.* 34, 68).

g. Relying upon the analogy or identity between these vegetable proteides and the animal substances of corresponding names, Liebig, in his memoir "On the Nitrogenous Food-stuffs of the Vegetable Kingdom," (*Ann. Pharm.* 39, 129) distinguishes:

1. As *Vegetable Albumin* or *Plant-albumin*, the proteide held in solution in aqueous plant-juices or extracts, which is not precipitated by acetic acid, but coagulates when heated.

2. As *Plant-fibrin*, the constituent of the seeds of cereals which is insoluble in water and in aqueous ammonia; it is wanting in leguminous fruits.

The plant-albumin and plant-fibrin of Liebig form therefore together, the plant-albumin of Berzelius.

3. As *Plant-casein* the constituent of leguminous fruits which dissolves in the cold aqueous extract, is not precipitated on heating this extract, but is precipitable by acetic acid; the precipitate is soluble in aqueous ammonia.

The legumin of Braconnot belongs, therefore, to Liebig's plant-casein. But Liebig further designates as plant-casein the constituent of the infusion of almonds which is precipitable by acetic acid as plant-albumin, and the constituent of the same extract coagulable by heat.

4. *Plant-gelatin* does not, according to Liebig, exist ready-formed, or only to a small amount, in the flour of cereals and leguminous fruits. It is a casein-compound containing acid; its solution in aqueous ammonia, heated to the boiling point, deposits a small coagulum when acetic acid is dropped into it.

h. Dumas & Cahours (*N. Ann. Chim. Phys.* 6, 385) use the names *plant-albumin* and *plant-fibrin* almost in the same sense as Liebig, excepting that they apply the former chiefly to the coagulum which separates from gluten-water when heated; the latter to that portion of the gluten which is insoluble in boiling alcohol. Their *plant-casein*, different from that of Liebig, is the portion of the alcoholic extract of gluten which separates on cooling, therefore perhaps the same as the gluten of Saussure; their *plant-glutin* is the substance which separates only on further concentration and cooling, therefore the mucin of Saussure.

The name *legumin* is applied by Dumas & Cahours to the constituent of leguminous fruits and oleaginous seeds which is precipitable by acetic acid, therefore Liebig's vegetable casein, as well as to the constituent of oleaginous seeds which is coagulable by heat, and therefore belongs, according to Liebig, to vegetable albumin.

i. Günsberg distinguishes in wheat-gluten: 1. A constituent not soluble either in alcohol or in boiling water: the *fibrin of gluten;* 2. A portion soluble in alcohol, insoluble in boiling water: *gluten-casein* or *gliadin;* 3. A portion soluble in alcohol and in boiling water: *gluten-gelatin.* When crude gluten is kneaded with cold alcohol of 60 p. c. as long as the extract is rendered turbid by water, and the residue is boiled, first with weak and then with strong alcohol, the fibrin remains. The united extracts filtered, distilled, and further concentrated, deposit on cooling a mixture of casein and gelatin, which may be freed from foreign constituents by cold water, and resolved by boiling with water into gluten-gelatin, which dissolves, and casein, which remains behind. The gluten-casein is obtained by evaporating the decoctions (Günsberg).

k. v. Bibra (*Die Getreidearten und das Brod*, Nürnberg 1860, 146) and Ritthausen (*J. pr. Chem.* 85, 193; 86, 257)—the latter, so long as he used boiling alcohol to decompose the wheat-gluten—likewise distinguish the insoluble portion as *plant-fibrin*, the constituents which pass into solution as *plant-casein* or *paracasein*, which separates in the first instance, and *plant-gelatin*, which does not separate even on concentration. Afterwards Ritthausen (*J. pr. Chem.* 91, 296) observed that this process gives rise to a transformation of soluble into insoluble constituents of the wheat-gluten; he therefore dissolved the gluten in water containing potash, precipitated with acetic acid, and decomposed the precipitate by treatment with cold alcohol. The substances thus obtained are designated as follows:

1. *Paracasein, Gluten-casein:* the portion insoluble in alcohol.

2. *Plant-fibrin, Gluten-fibrin:* the portion which first separates from the alcoholic solution.

3. *Mucin, Mucedin:* a portion precipitable from the mother-liquor by absolute alcohol.

4. *Plant-gelatin, Gliadin:* the portion which remains in solution.

The *legumin* of leguminous-fruits, or pulse, approaches very nearly to gluten-casein; almonds and lupines contain *conglutin*, a substance different from legumin.—Rye, maize, and oats contain substances agreeing almost exactly: the two constituents of rye with gluten-casein and mucedin; the chief constituent of maize with gluten-fibrin; a subordinate constituent with conglutin; that of oats with legumin (Ritthausen).

l. Commaille distinguishes five constituents of gluten insoluble in cold water, namely: 1. *Sitosin* (albumin of flour) soluble, like all the other constituents of gluten, in alkaline water, and precipitated by acids: the aqueous solution coagulates when heated, and gives with hydrochloric acid and mercuric chloride precipitates which redissolve in a large quantity of acid. The pale-yellow platinum-compound contains 7·14 to 7·39 p. c. platinum. — 2. *Imesin* (fibrin, Ritthausen's gluten-casein). Dissolves after drying only in water containing 0·1 p. c. hydrochloric acid. The platinum precipitate contains 7·15 to 7·33 p. c. platinum. — 3. *Sitesin* (gluten-casein, Ritthausen's plant-fibrin). Dissolves in water containing 0·1 p. c. hydrochloric acid; a larger proportion of the acid precipitates it at first, and afterwards redissolves it; mercuric chloride does not precipitate the solution; platinic chloride forms an orange-yellow precipitate containing when dry 5 21 to 5·48 p. c. platinum. — 4. *Glutin.* Nearly insoluble in acidulated water; very sparingly soluble in acetic acid, easily in strong hydrochloric acid, not miscible with water; dilute alcohol forms with it an emulsion, from which a large quantity of water throws down a coagulum. A large quantity of ether likewise coagulates the emulsion and dissolves out a yellow oil, the glutin thus coagulated dries up to a translucent, white friable mass, which imparts to water the property of frothing strongly, but scarcely dissolves in it; from the filtrate, platinic chloride throws down a nearly white precipitate containing 2·57 p. c. platinum; this platinum-compound is precipitated from the alcoholic solution by water, and becomes elastic and iridescent in ether, but does not dissolve. — 5. *Mucin.* Dissolves easily, even after drying, in water and cold alcohol of 80 p. c. The acidulated solution is precipitated by mercuric chloride; the dark yellow glutinous platinum precipitate contains 5·37 p. c. platinum (Commaille *J. Pharm.* [4], 4, 108; *Chem. Centr.* 1867, 585; *Jahresb.* 1866, 710).

m. To all these views is opposed that of Denis, according to which plants contain only one proteide or albuminous substance, namely, an insoluble substance, Denis's *glutin*, by the transformation of which the others are produced. Glutin is obtained from peas, beans, lentils, and wheat-flour, but best of all from sweet almonds. Peeled almonds are triturated with 16 pts. water, and the pulp separated from the emulsion is pressed and diffused, to a pasty consistence, in a 10 p. c. solution of common salt. The mass diluted with water after some hours is filtered, and the glutin is precipitated from the filtrate by addition of a large quantity of water.

Moist glutin dissolves easily in salt water of 10 p. c. forming a solution which is rendered turbid by saturation with powdered common salt or sulphate of magnesia, but not quite precipitated by the latter salt, like a solution of fibrin. The solution is precipitated by alcohol and coagulated by heat.

The solution of glutin in salt water exhibits the reactions of plant albumin, especially if slightly acidulated, or neutralised by alkalis. Dried glutin treated with salt water leaves a portion having the properties of gluten. Hot water alters glutin, and imparts to it the properties of the plant-casein of Scherer and Jones; hot aqueous alcohol dissolves it partially, and separates it in the form of Dumas' plant-casein; the undissolved part is Dumas' plant-fibrin. When the alcohol is evaporated, Dumas' glutin remains behind. Legumin and amandin are likewise obtained from glutin when the latter is subjected to the treatment described for the preparation of these substances.

The emulsion of sweet almonds contains the same glutin, which is dissolved with the aid of salts and partly of alkalis. If the oil-drops diffused through the emulsion be separated by rapid filtration, a transparent liquid is obtained, which is not precipitated by water alone, but yields a precipitate of glutin with dilute hydrochloric or acetic acid after previous dilution with 5 vol. water (Denis, *Mémoire sur le sang*, Paris, 1859, 170)

In the following description of the individual vegetable proteides, Ritthausen's views and nomenclature are for the most part followed, but it has been thought necessary, for the most part, to describe separately the substances originating from different plant-organs (Kr.).

Plant-albumin.

SCHEELE. *Opusc.* 2, 103.—FOURCROY. *Ann. Chim.* 3, 252.—JORDAN, *Scher. J.* 5, 331.—PROUST, *J. Phys.* 56, 97; *Gilb.* 15, 278.—SEGUIN. *Ann. Chim.* 92, 5.—EINHOF. *A. Gehl.* 4, 461; 6, 63 and 116.—LINK, *Schw.* 14, 294.—TADDEI, *Brugn. Giorn.* 12, 327.
BOUSSINGAULT. *Ann. Chim. Phys.* 65, 305; *Berzel. Jahresber.* 18, 327.
LIEBIG. *Ann. Pharm.* 39, 142; *Berzel. Jahresber.* 22, 266.
JONES. *Ann. Pharm.* 40, 66; *Berzel. Jahresber.* 22, 266.
DUMAS & CAHOURS. *N. Ann. Chim. Phys.* 6, 409; *Berzel. Jahresber.* 23, 588.
RÜLING. *Ann. Pharm.* 58, 306.

Vegetable albumin. Pflanzeneiweiss. The nitrogenous substance occurring in plant-juices, or extractable by cold water from dry plant-organs; coagulable by heat; not precipitable by acetic acid. Compare p. 422.

Until further investigation shall have decided the question, it must remain doubtful whether the substances prepared from different plants as plant-albumin, are identical or not. Moreover, the property of separating out from aqueous plant-juices when heated, might be imparted to the other known vegetable proteides by the presence of acids or salts in the juices (Kr.).

Preparation. The filtered wash-water obtained in the preparation of wheat-gluten deposits on boiling a coagulum which may be dried in a vacuum (Boussingault). Dumas & Cahours free the coagulum from starch by treating it with diastase at 75°, and exhausting with alcohol and ether.

The plant-albumin analysed by Liebig, Jones, and Rüling was likewise separated by heating the cold aqueous extracts; that from peas, after precipitation of the legumin with acetic acid. A product obtained from gluten, and analysed by Wall & Varrentrapp, is likewise referred by Liebig to plant-albumin (s. GLUTEN).

When potatoes cut into slices are drenched with water containing 2 p. c. sulphuric acid, the liquid after 24 hours poured upon fresh potatoes, and this operation repeated, a solution is obtained, which after neutralisation with potash, deposits large flocks of plant-albumin on boiling (*Handworterb.* 2, 2, 2, 147).

Properties. Amorphous mass resembling coagulated egg-albumin.

Plant-juices have a neutral or acid reaction, not alkaline like solutions of animal albumin (Dumas & Cahours).

	Boussingault. *Wheat.*	Liebig. *Wheat.*	Jones. *Rye.*	*Almonds.*	Dumas & Cahours. *at* 140°. *Wheat.*	Ruling. *at* 100°. *Peas.*	Ruling. *at* 140°. *Potatoes.*
C	52 49	53·97	53 71	55·96	53·74	52 45	53 81
N	18 40	15 92	15·85	13 75	15·65		
H	6 90	7 23	7 77	7·53	7·11	6 81	7 32
O	22 21	22·88	22 67	22·76	23·50		
	100 00	100 00	100 00	100 00	100·00		

After deduction of 1 p. c. ash (Boussingault), of 8 5 p. c. (Dumas & Cahours), of 0 89 and 1 40 p c. (Ruling). The albumin of peas contains 0 80, that of potatoes 0·98 p. c. sulphur (Ruling); that of peas contains 0 80, that of wheat 1·04, that of rye 0 77 p. c. sulphur (Mulder, *Scheik. Onderzoek,* 4, 404; *J. pr. Chem.* 44, 503).

The albumin of plant-juices coagulates at 50°—60° (Proust), that of wheat at 80° (Boussingault). — The tubers of *Dioscorea Batatas* contain a peculiar vegetable albumin which coagulates only after prolonged boiling (Frémy, *Compt. rend.* 40, 128).

When kept in the moist state, it passes into stinking *putrefaction*, accompanied by evolution of gas, and formation of leucine, together with the same volatile products that are evolved from cheese (Liebig). — Coagulated plant-albumin dissolves in *oil of vitriol* with red-brown colour; in fuming *nitric acid*, with formation of oxalic acid (Link). It dissolves in warm concentrated *hydrochloric acid* with black to violet blue colour (Liebig). The albumin of cabbage forms with *chromic acid* a dark yellow curd (Hünefeld, *J. pr. Chem.* 9, 30).

The albumin dissolved in plant-juices is precipitated by *acids*, *salts*, and *alcohol* (Proust). It is not precipitable by *acetic acid* (Liebig). Albumin prepared from potatoes with water containing sulphuric acid, does not coagulate when its ammoniacal solution is boiled, but acetate of ammonia precipitates the solution even in the cold, and more abundantly when heated, so that the filtrate is no longer clouded by acetic acid (Löwenberg).

Plant-albumin dissolved in ammonia is precipitated by *oxalate of ammonia* even in the cold, the filtrate being precipitable by acetic acid; by *nitrate of ammonia* only at the boiling heat; by sulphate of ammonia, sulphate of soda, and chloride of sodium, completely in the cold (Löwenberg, *Pogg.* 78, 327).

The albumin of potatoes dissolves in *potash-ley* and is precipitated therefrom by acids. When boiled with alcoholic potash, it gives off 1·3 to 2 p. c. of its weight of ammonia (R. Theile, *Chem. Centr.* 1867, 385). — Gluten-albumin separated by heating dissolves partially while fresh, in moderately diluted aqueous *saltpetre*, the solution being rendered turbid by hydrochloric acid. It does not harden with mercuric chloride (v. Bibra).

Legumin.

Einhof. *A. Gehl.* 6, 126 and 548. — Braconnot, *Ann. Chim. Phys.* 34, 68; *Mag. Pharm.* 18, 59; *Repert.* 26, 258. — *Ann. Chim. Phys.* 43, 347.

Liebig. *Ann. Pharm.* 30, 138; *Berzel. Jahresber.* 22, 266.

Dumas & Cahours. *N. Ann. Chim. Phys.* 6, 423; *Berzel. Jahresber.* 23, 591.

Rochleder. *Ann. Pharm.* 46, 155; *Berzel. Jahresber.* 24, 461.

Noad. *Chem. Gaz.* 1847, 357; *Pharm. Centr.* 1847, 862; *Lieb. Kopp. Jahresber.* 1847–1848, 842.

Norton. *Sill. Am. J.* [2], 5, 22; *Pharm. Centr.* 1848, 241; *Lieb. Kopp. Jahresber.* 1847—1848, 843.

Löwenberg. *Pogg.* 78, 327.

Ritthausen. *J. pr. Chem.* 103, 65, 193 and 273; *Chem. Centr.* 1868, 501.

First distinguished by Einhof in 1805; named by Braconnot. Belongs, together with other proteides precipitable by acetic acid, to Liebig's plant-casein, and together with conglutin, to the legumin of Dumas & Cahours (p. 424).

Occurrence. In the seeds of leguminous plants, especially in peas, beans, vetches, and lentils. — Distinguished, according to Ritthausen's earlier experiments, from the conglutin of (almonds and) lupines, by its reaction with boiling sulphuric acid, with which it forms *legamic acid*, but no glutamic acid. Subsequently, however, Ritthausen (*J. pr. Chem.* 106, 445; 107, 218) found that the so-called legamic acid is a mixture of aspartic acid with glutamic acid, whence it appears that the supposed difference between legumin and conglutin has no existence.

Preparation. The pulverised seeds are macerated for six hours at 4° to 8°, in 7—8 times their weight of water, which is rendered slightly alkaline in case the seeds have an acid reaction; the liquid is then poured off; the deposit again treated with 4 or 5 pts. of water and left to settle at 4° to 5°; and the liquid again poured off is precipitated with acetic acid of 11 p. c. The precipitate is collected in the cold, drenched with alcohol of 45 p. c., which causes it to agglutinate, then removed from the filter, and washed successively with weak and with stronger alcohol, with ether, and again with alcohol. If the legumin thus obtained forms, when boiled with a mixture of equal masses of oil of vitriol and water, a turbid solution which deposits black-brown flocks on dilution with water, but not a clear brown solution as pure legumin does, it must be further purified by solution in water containing 0·1 to 0·2 p. c. potash, and precipitation with acetic acid. It is dried in a vacuum over oil of vitriol and afterwards in the water-bath, to ensure the complete removal of the alcohol (Ritthausen). The bruised peas may also be repeatedly boiled with a large quantity of alcohol, the legumin extracted from the residue by alkaline water, and the precipitate treated with alcohol and ether (Ritthausen).

Ritthausen recognises the purity of legumin, not only by its behaviour to boiling sulphuric acid diluted to one-half (*vid. sup.*), but also: 1. By its perfect solubility in alkaline water; impure legumin would form a turbid solution. — 2. By its reaction with cuprate of potash. When alkaline legumin is mixed with a small quantity of cupric sulphate and then with potash-ley, a clear reddish-violet liquid is formed if the legumin is pure; whereas legumin containing starch or gum, forms a blue, sometimes turbid liquid.

2. Shelled peas are washed with warm water as long as the liquid is thereby coloured, then triturated with ammoniacal water; the liquid is precipitated with acetic acid; and the precipitate is washed, out of contact of air, with water, alcohol, and ether. Legumin thus prepared still contains foreign substances, which may be removed by dissolution in strong potash-ley, precipitation of the filtrate with acetic acid, washing, redissolution in aqueous ammonia, and precipitation with acetic acid (Rochleder).

3. Löwenberg dissolves the legumin precipitated by acetic acid from infusion of peas, and washed till the wash-water exhibits an alkaline reaction, in aqueous ammonia; strains; warms the liquid till the excess of ammonia is expelled; mixes it with common salt, and boils, whereby albumin is precipitated. From the filtrate acetic acid precipitates the legumin, which must be thoroughly washed with cold water and treated with boiling alcohol and ether. By this treatment albumin, and a body soluble in water but insoluble in acetic acid, are removed (Löwenberg).

Braconnot triturates macerated peas with cold water; leaves them to settle; and evaporates the liquid, whereupon the legumin separates in greenish mucous films, which are purified by washing with water and boiling with alcohol. Or he precipitates the aqueous extract with nitric acid; exhausts the precipitate with boiling alcohol; dissolves it in boiling water with the aid of a little ammonia; boils till the greater part of the ammonia is volatilised; and precipitates with alcohol. — Liebig and Jones precipitate with sulphuric acid, and exhaust the precipitate with ether after washing it with water. Dumas & Cahours precipitate with very dilute acetic acid, not in excess; wash the precipitate with water, alcohol, and ether, and dry it in a vacuum at 140°. — Theile precipitates the extract of peas, clarified by deposition, with alcohol. Noad and Norton purify it by solution in ammonia and precipitation with acetic acid.

Properties. Amorphous, white, loose, friable mass (Ritthausen); that prepared by other methods is often coloured. Legumin precipitated from concentrated solutions by acids, has a moist pearly lustre; dilute solutions yield it in flocks (Dumas & Cahours). It has always an acid reaction, probably due to the presence of phosphoric acid (Einhof; Ritthausen). Braconnot's legumin is neutral or alkaline.

Legumin from Peas.

	Dumas & Cahours. *at* 140°.	Rochleder. 130°.	Rüling. 100°.	Noad. 100°.	Norton. *at* 130°.	
C	50·53	54·05	50·59	50·78	50·72	50·57
N	18·15	14·78	16·54	15·94	15 77	16·84
H	6·91	7·40	6·83	7·88	6·56	6·90
S			0·47		0·77	0·33
O			25·57			
Ash	1·90	7·12	0·60		0·77	1·23
PO^5 *a* PO^5 *b*					2·31P	1·66P

Legumin from Peas.

	Ritthausen.		
	mean.	*max.*	*min.*
C	51·47	51·87	50·74
N	16·82	17·22	16·36
H	7·02	7·32	6·92
S	0·40	0·45	0·33
O	21·29		
Ash	2·27	3·58	1·70
PO^5 *a.*	0 64	0·77	0·48
PO^5 *b.*	1·74	2·33	1·73

Legumin from Beans, Vetches, Lentils.

	Jones.	Rochleder. *at* 130°.	Rüling.	Noad. *at* 100°.
C	54·30	51·65	51·14	53 57
N	15·89	14·41		15·26
H	7·59	6·74	7·04	7·79
S			0·45	
Ash		1·91		

	Ritthausen.				
	a.	*b.*	*c.*	*d.*	*e.*
C	51·48	51·14	51 10	51.61	52 53
N	14·71	16·87	17·11	16·61	16·49
H	6·96	7 06	7·11	6 86	6·84
S	0·45	0·10	0·40	0·37	0·40
O	26·35	21·53	23·98	21·55	23·74
Ash	3·55	2 65	2·92	1·97	
PO^5 *a.*	1·29	0 89	0·43	0·61	3·10
PO^5 *b.*	2·19	2·27	1 32	1·04	

The analyses by Varrentrapp (*Ann. Pharm.* 39, 145, and 291), Scherer (*Ann. Pharm.* 39, 146, 40, 8), Mulder (*J. pr. Chem.* 44, 503) and Theile are not given.—The latter analysed legumin containing 7·88 p. c. ash.

Dumas & Cahours analysed legumin from lentils, white beans (17·58 p. c. N.), and white mustard, with nearly the same results.—Noad also dried the legumin, which he analysed at 150°, and then found 50·40 p. c. carbon (peas), and 55·05 p. c. carbon (beans); the amount of nitrogen in his analyses above cited, probably refers to the product dried at these temperatures.—The analyses in the second table, by Jones, Rochleder, Rüling, and Noad, refer to legumin from white beans, those by Ritthausen, *a.* to legumin from white garden-beans (the legumin in which appears, therefore, with otherwise similar composition, to contain 2 p. c. nitrogen less than legumin from peas); *b.* from black vetches; *c.* from broad-beans; *d.* from horse-beans; and *e.* from lentils. Ritthausen dried his legumin at 130°.

Legumin contains phosphoric acid, either as an essential constituent, or at all events not in combination with bases, the amount of ash being very small, if care be not taken to prevent volatilisation of phosphoric acid.—The total quantity of ash is but little greater than that of the phosphoric acid; the remainder consists of potash, with very small quantities of lime, magnesia, and oxide of iron.—The phosphoric acid is either (PO^5,*a*) precipitable from the hydrochloric acid solution of legumin by ammoniacal magnesia salt, or (*b*) not precipitable. Unoxidised phosphorus, supposed to exist in legumin by Mulder, Norton, and Voelcker (*J. pr. Chem.* 75, 320) is not present (Ritthausen). Löwenberg's pea-legumin (with 53·89 p. c. C., 7·26 H., 0·30 S.) is, according to his statement, free from phosphorus.

Decompositions and Combinations. — Legumin subjected to *dry distillation*, melts, and yields, with tumefaction (without it, according to Rochleder), a small sublimate of carbonate of ammonia, a copious yellow distillate containing carbonate of ammonia with small quantities of acetate and hydrosulphate, and leaves (phosphoretted) charcoal (Braconnot). — It is insoluble, or very nearly so, in water, and is rendered insoluble in acids and alkalis by boiling with water (Ritthausen). Löwenberg's legumin forms, when boiled with water, a body soluble in water, and precipitable by acetic acid.

The oft-repeated statement that legumin is soluble in cold water would seem to imply that it must exist in solution in the aqueous extract of pulse. It is held in solution through the medium of the inorganic constituents (Rochleder), of phosphoric acid, or of potash combined with legumin (Ritthausen).

Behaviour of the Aqueous Extract of Pulse. — The extract remains turbid, even after repose, both because it contains suspended fat, and because it becomes acid on standing, and in consequence deposits plant-casein (legumin) (Liebig).

According to Liebig, it does not coagulate when heated, but when evaporated, forms, like animal milk, a scum which is renewed after removal. Alcohol and all acids cause the extract to curdle; oxalic acid and tartaric acid added in excess redissolve the precipitate, but the resulting solution is reprecipitated by nitric or sulphuric acid; excess of acetic acid does not dissolve the precipitate. These precipitates are compounds of legumin with acids (Liebig). The precipitate formed by sulphuric acid is free from that acid after washing (Jones).

According to Löwenberg, extract of peas, prepared in the cold and then neutral, contains, in addition to true legumin, a substance likewise precipitable by acetic acid, and moreover coagulable at the boiling heat (albumin), together with a third body soluble in water but insoluble in aqueous acetic acid.

Extract of peas, prepared at 0°, coagulates when heated, and the filtrate is further precipitated by acetic acid. If it be precipitated in the first instance by acetic acid, and the filtrate neutralised with carbonate of ammonia and boiled, it deposits only a small quantity of coagulum. — If the precipitate formed by acetic acid be washed beyond the point at which the wash-water appears neutral, a liquid precipitable by acetic acid runs through the filter, whilst the precipitate which remains on the filter dissolves partially at first, and afterwards almost entirely in acetic acid (Löwenberg).

The aqueous extract of pulse, left to itself at 15° to 20°, turns sour from formation of lactic acid, and coagulates in 24 hours, with slight evolution of gas, and separation of a curdy jelly of lactate of legumin. This jelly has an acid reaction, even after prolonged washing; it dissolves easily in aqueous ammonia and the fixed alkalis, and converts cane-sugar at a gentle heat into acetic acid, lactic acid, and a gum (Liebig). Moist legumin, kept in a warm place, passes into putrefaction with appearances similar to those exhibited by cheese, but without forming products which blacken silver.

The aqueous extract of pulse leaves, when ignited, an alkaline ash containing potash and phosphoric acid. It is not precipitated by lime-salts or sulphate of magnesia in the cold, but gives a precipitate with these reagents when gently heated. Under all these circumstances vegetable casein reacts in the same manner as animal casein (Liebig).

Legumin dissolves in cold *oil of vitriol;* the viscid solution when heated in the water-bath, becomes mobile, dark purple-coloured, and no longer precipitable by water. By prolonged boiling of legumin (from hog-beans) with moderately dilute sulphuric acid, there are formed: leucine, and a small quantity of ammonia (Braconnot); also tyrosine, glutamic acid, active aspartic acid (Ritthausen's former legamic acid), and amorphous brown substances (Ritthausen). The solution in *nitric acid* leaves on evaporation, oxalic acid and a yellow body having a harsh and bitter taste (Braconnot). — Dissolves completely in fuming *hydrochloric acid*, after boiling for 15 to 20 minutes, forming a brown liquid not precipitable by excess of ammonia (Ritthausen).

Iodine appears to render legumin soluble in water; on heating the solution, a yellow iodated precipitate is formed, which, when washed with boiling alcohol and dried, turns starch blue and gives off iodine when heated. It is insoluble in boiling water, but dissolves easily and without coloration in aqueous ammonia, and is precipitated by nitric acid (Braconnot).

Heated with *bichromate of potash* and *sulphuric acid*, legumin yields prussic acid, bitter almond oil, and benzoic, formic, and other volatile fatty acids: also acetonitrile and valeronitrile (Fröhde, *J. pr. Chem.* 77, 290).

Dissolves easily in dilute *ammonia-water*. On exactly neutralising the solution with acetic acid and boiling, the liquid coagulates, and does not retain in solution any substance precipitable by acetic acid. If the ammoniacal solution be left to evaporate at a low temperature, the whole of the protein-substance separates as a scum (Löwenberg).

Legumin dissolves very easily in dilute *potash* or *soda-ley*. Water containing one or two thousandths of potash-hydrate, dissolves pulverised legumin completely in a day or two, without turbidity or decomposition (Ritthausen). By repeated solution in (stronger) potash-ley and precipitation with acetic acid, sulphuretted hydrogen is each time evolved (Rüling). The solution in potash-ley, exposed to the air for 8 to 10 days, gives off ammonia and deposits white flocks; after this it does not evolve ammonia on boiling, till it has been concentrated so far as to solidify on cooling. If it be continually boiled and the water renewed, brown flocks are separated, and a brown solution is formed, from which acetic acid separates grey flocks (Rochleder). When the boiling is continued for eleven hours, at intervals of a week, about 3 p. c. of the legumin goes off as ammonia (Theile, *Jenaer Zeitschr.* 4, 264; *Chem. Centr.* 1868, 691).

Dissolves in aqueous *carbonates* and *phosphates of the alkalis*, forming a turbid liquid (Ritthausen).

Legumin precipitated by acetic acid and dissolved in ammonia, is precipitated by *oxalate*, *nitrate*, and *sulphate of ammonia*, not in the cold, but on boiling; by *chloride of sodium* or *sulphate of soda*, not even at the boiling heat (Löwenberg).

Dissolves in cold, very dilute *lime-* and *baryta-water*, forming a [illegible]y, frothing liquid, which coagulates on boiling, and is then but [illegible] precipitated by acids. The solution is precipitated by mineral acids (even by carbonic acid, Einhof), and by vegetable acids not in excess; also by alcohol.—Legumin precipitated by sulphuric acid, and suspended in water so as to form a milk, produces a thick curd when boiled with *carbonate of lime*, *baryta*, or *magnesia*. Legumin suspended in water, coagulates when boiled with *gypsum-water* (Braconnot).

On agitating an alkaline solution of legumin with a small quantity of *cupric sulphate* and potash, a clear violet or reddish-violet solution is formed; with impure legumin, however, it is blue and turbid (Ritthausen). *Mercuric chloride* and many other metallic salts coagulate legumin suspended in water (Braconnot). Mercuric chloride produces a precipitate insoluble in hydrochloric acid (Commaille).—*Bichloride of platinum* throws down from an alkaline solution of legumin, a precipitate containing 5 p. c. platinum; from legumin prepared with hydrochloric acid, a platinum-salt is obtained, containing 9·8 to 10 p. c. platinum (Commaille).

Moderately dilute *acetic acid* dissolves legumin (Einhoff; Ritthausen); according to Liebig and Rochleder, it does not. The precipitate thrown down by acetic acid from legumin-solutions dissolves in excess of the acid (Löwenberg).

Legumin dissolves easily in aqueous *oxalic*, *tartaric*, and *citric* acid. The dilute solutions have a scarcely perceptible sour taste; they are precipitated by mineral acids, also by nitrate of baryta, nitrate of lime, nitrate of lead, ferrous sulphate, cupric sulphate, and tincture of galls; not by acetate of baryta, alumina or lead, by mercuric chloride, or by alcohol (Braconnot).

Insoluble in *alcohol* (Braconnot) (comp. p. 423), *ether*, and *volatile oils*. *Tincture of galls* does not precipitate solutions of legumin (Braconnot).

Appendix to Legumin.

1. Almond-legumin.

Proust. *J. Phys.* 54, 199; *A. Gehl.* 5, 596.—Buchholz, *A. Gehl.* 6, 617.—A. Vogel, *Schw.* 20, 64.—Boullay. *Ann. Chim. Phys.* 6, 40.—Pfaff. *Materia Medica*, 6, 136.—Soubeiran, *J. Pharm.* 12, 52.—Payen & O. Henry. *J. Chim. méd.* 2, 156.

Dumas & Cahours. *N. Ann. Chim. Phys.* 6, 423.

Mulder. *Scheik. Onderz.* 4, 404; *J. pr. Chem.* 44, 503.

Norton. *Sill. Am. J.*, [2], 5, 22; *Pharm. Centr.* 1848, 241; *Lieb. Kopp's Jahresb.* 1847—1848, 843.

Bull. *Ann. Pharm.* 69, 145; *Pharm. Centr.* 1849, 353; *Lieb. Kopp's Jahresb.* 1849, 495.

Ritthausen. *J. pr. Chem.* 103, 78, 193, and 273; *Zeitschr. f. Chem.* [2], 6, 126.

The seeds of many plants belonging to other families, when treated like leguminous fruits for the preparation of legumin, yield substances very closely allied to legumin, but exhibiting certain diversities in their composition, and perhaps also in their reactions.

To this head belongs the proteide of the oleaginous, emulsion-forming seeds, the *Emulsin* of the third edition of this handbook, the *Amygdalin* of Döbereiner, which Dumas & Cahours regard as legumin.

a. From sweet almonds, the kernels of plums, apricots, hazel-nuts, and white mustard, one and the same proteide is obtained, identical in properties and composition with the legumin of pulse. According to Liebig (p. 423) oleaginous seeds contain plant-albumin and plant-casein; according to Löwenberg, sweet almonds, like peas, contain three different proteides (p. 423).

b. The legumin of sweet and bitter almonds is richer in nitrogen than that of pulse, and exhibits, even to the amount of sulphur, the composition of legumin from yellow lupines (Ritthausen).

Ritthausen designates the legumin of almonds and of lupines as *conglutin.* According to his earlier statements, this proteide is to be distinguished from legumin, because, when boiled with dilute sulphuric acid, it yields, besides aspartic acid and the other products of legumin, 5 to 6 p. c. of glutamic acid. This reaction, however, has not been established, either for the conglutin of almonds, or for that of maize (*infra*), but only for that of yellow lupines; moreover Ritthausen has more recently obtained both these acids from the legumin of hog-beans.

	Dumas & Cahours.			Ritthausen. *At* 130°.				
	at 140°.	Norton.	Bull.	*a.*	*b.*	*c.*	*d.*	*e.*
C	50 90	50·74	51·02	50·24	50·63	50·83	50·66	51·41
N	18 93	17·24	15 80	18·37	17·97	18 40	16·65	17·72
H	6·72	6·60	6·87	6·81	6·88	6·92	7·02	7·19
S	....	0·30	0·57	0·45	0·40	0·91	0·45	
O	....		25·74	24·13	24·12	23·24	25·21	
Ash	....	0·26	1·59	2·66	1·23	1·45	1·71	
PO^5, *a.*	....	0·81	....	2·38	0·31	0·48	1·53	
PO^5, *b.*	....	....	....		0·89	0·96		

From sweet almonds (Norton, Bull, Dumas, & Cahours). The latter examined also, with nearly the same results, legumin from palm-kernels, apricot-kernels, hazel-nuts, and white mustard. A second sample of legumin contained 16·75 p. c. N. (Bull).—*a,* From sweet; *b,* from bitter almonds; *c,* from yellow; *d,* from blue lupines; in the last cases the purification was perhaps not quite perfect; *e,* from maize-flour, which had been freed from maize-fibrin by warm alcohol, then exhausted with water containing potash, and precipitated with acetic acid (Ritthausen, *J. pr. Chem.* 106, 488).

See also the remarks on the analyses of legumin (p. 430).

Conglutin in the moist state is more glutinous, and more soluble in acetic acid then legumin, but exhibits the same reactions, especially towards water, very dilute aqueous ammonia, potash, and soda, and concentrated hydrochloric acid (Ritthausen).

Almond-legumin is precipitated, according to Norton, from the ammoniacal solution by neutral acetate of lead, whereas the ammoniacal solution of pea-legumin is merely clouded by that salt.

When conglutin from lupines is boiled for ten or twelve hours with 3 pts. oil of vitriol and 6 pts. water in a flask with reversed condenser, and the solution freed from sulphuric acid is concentrated, tyrosine, leucine, and glutamic acid crystallise out from it successively as it cools. The mother-liquor, which is still strongly acid, deposits, when neutralised with carbonate of baryta and mixed with alcohol, gluta-mate of baryta mixed with aspartate; and the filtrate when freed from alcohol by distillation and concentrated, yields a body resembling leucine, from which, by boiling out the finally remaining brown viscid mass with absolute alcohol, and cooling, an additional quantity of lupine-conglutin may be obtained. It forms white flocks containing 48·21 p. c. C., 7·59 H., 13·02 N. Lastly there remains a brown viscid residue, insoluble in absolute alcohol (Ritthausen, *J. pr. Chem.* 103, 234; 106, 445; 107, 218).

Almond-legumin, Commaille's *amandin*, purified by precipitating filtered almond milk with hydrochloric acid, dissolving in alkaline water, and reprecipitating with hydrochloric acid, gives with *bichloride of platinum* a precipitate containing 7·02 to 7·45 p. c. platinum; its hydrochloric solution is precipitable by mercuric chloride (Commaille, *J. Pharm.* [4], 4, 108; *Jahresb.* 1866, p. 710).

Other statements respecting differences between almond-legumin and the legumin of pulse, appear to be founded on misconceptions arising from the fact, that statements actually relating to the behaviour of the aqueous extracts of peas and almonds have been erroneously regarded as applicable to the isolated substances (Kr.).

When concentrated seed-milk is freed from oil by agitation with ether, and the lower watery layer is separated and heated to the boiling point, coagulated plant-albumin separates out, whilst plant-casein precipitable by acetic acid remains in solution. On the other hand, acetic acid, added to the cold aqueous extract of almonds freed from oil, throws down plant-casein, whilst plant-albumin remains dissolved (Liebig).

Similar observations had previously been made by Payen, O. Henry, and Gmelin.

To this head also belong the statements of Dumas & Cahours on the reactions of legumin, all of which refer to the substance precipitated by acetic acid from infusion of sweet almonds.

This *almond-legumin* is separated as a coagulum by heating the aqueous extract, as a pearly-lustrous precipitate by precipitation with acetic acid, and in flocks by dilution. Orthophosphoric acid and other mineral acids likewise precipitate it from the extract of almonds. Strong nitric acid dissolves dry almond-legumin, with evolution of red vapours; oil of vitriol dissolves it slowly, yielding a brown solution without formation of glycocoll; strong hydrochloric acid dissolves it with fine blue-violet colour.—It dissolves in aqueous alkalis when heated, with evolution of ammonia; easily in cold ammonia-water and in boiling baryta- and lime-water.—In strong acetic acid it swells up to a translucent jelly, and dissolves on addition of boiling water, the solution leaving on evaporation a gum soluble in water and having the same composition as almond-legumin.

Almond-legumin does not dissolve either in cold strong alcohol or in weak boiling alcohol. It is insoluble in ether. The aqueous infusion of almonds left in contact for 24 hours with infusion of rennet deposits coagulated almond-legumin as a gummy mass; no substance soluble in acetic acid remaining in solution. This coagulum contains 50·41 p. c. C., 19·00 N., 6·92 H., 23·67 S. and O. (Dumas & Cahours).

2. Avenin, or Oat-legumin.

NORTON. *Sill. Am. J.* [2], 5, 22; *Lieb. Kopp Jahresb.* 1847–48, 844.
KREUSLER. *J. pr. Chem.* 107, 17; *Chem. Centr.* 1869, 609.

First distinguished by Johnston. — Occurs in oats, together with vegetable gelatin.

Preparation. 750 grms. of finely bruised oats are drenched with a mixture of 5 litres of water and 3 grms. of potash-hydrate; the liquid is left to itself for 12 hours in the cold, and then strained; the residue is washed with water and left to settle, and the turbid brown liquid drawn off from the deposit of starch is precipitated with dilute acetic acid. The greyish-white precipitate, after it has settled down, is collected, washed on a filter with alcohol of 80 p.c., whereby it is rendered compact and separable from the filter, then exhausted with strong alcohol, and finally with ether. For dehydration it is freed as much as possible from ether by pressure, then drenched with absolute alcohol, and left at rest for 12 to 24 hours, after which it is dried over oil of vitriol, and finally in the water-bath. Avenin thus prepared still retains starch, which may be removed by dissolving the avenin in water containing $\frac{1}{10}$ p. c. potash-hydrate, and precipitating the clarified solution with acetic acid. Oatmeal previously exhausted with cold or hot alcohol may be used in the preparation instead of fresh oatmeal.

Avenin prepared as above, especially that which is obtained from fresh oatmeal, still retains vegetable gelatin, which lowers its amount of nitrogen by nearly ½ p.c., and increases the carbon in the same proportion. It may be purified by repeated boiling with alcohol of 60 p.c., but then almost entirely loses its solubility in dilute potash and acetic acid (Kreusler).

Properties. Loose, easily friable mass, having an earthy aspect, and white colour inclining to grey; in other respects it exactly resembles legumin prepared in a similar manner (Kreusler).

	Norton.		Kreusler.
	a.	*b.*	*mean, at* 140°.
C	52·36	51·82	51·63
N	14·76	16·39	17·16
H	6·85	6·86	7·49
S	1·06	1·11	0·79
O	24·16	22·82	22·93
	99·19	99·00	100·00

Norton's avenin (*a*) was precipitated from aqueous extract of oats by acetic acid, and purified by solution in ammonia, precipitation with acetic acid, and exhaustion with alcohol and ether; *b* was extracted by ammoniacal water from oats previously exhausted with water, precipitated and purified in a similar manner. It still retained 0·75 and 0·86 p. c. ash, 0·81 and 1·00 phosphorus (Norton). Kreusler's avenin contained 1·56 p. c. ash, and 1·36 PO^5, both of which are deducted.

Avenin exactly resembles legumin in its behaviour to solvents and precipitants; it does not dissolve in *water*, either cold or boiling, but swells up strongly in the latter; on the other hand it dissolves slowly in strong *hydrochloric acid*, the solution gradually turning reddish-blue; in *oil of vitriol* diluted with an equal volume of water, the solution becoming dark red-brown on boiling. It is nearly insoluble in aqueous *oxalic acid*, dissolves easily in warm aqueous *tartaric acid*, and when freshly precipitated, easily also in *acetic acid*, and is precipitated in its original state on neutralising the solution with an alkali. — It dissolves slowly but abundantly in water containing $\frac{1}{10}$ p. c. *potash-hydrate;* the solution is brown, yields a greyish-white flocculent precipitate with acetic acid, and, if previously boiled, gives off at the same time the odour of sulphuretted hydrogen. Avenin boiled with water is insoluble in acetic acid and in potash, but swells up to a jelly in acetic acid. *Alkaline phosphates* likewise dissolve avenin; *ferrocyanide of potassium* precipitates it from the acetic, not from the alkaline solution (Kreusler).

3. Glutamic acid, $C^{10}NH^9O^8$.

Ritthausen. *J. pr. Chem.* 99, 6, and 454; 107, 218.

Formation. By boiling plant-fibrin, mucedin (from wheat or rye), legumin, conglutin, or gluten-casein with dilute sulphuric acid; mucedin thus treated yields about 30 p. c. of glutamic acid.

Preparation. 1. Two pts. of plant-fibrin or mucedin are boiled with 5 pts. oil of vitriol and 13 pts. water for 24 hours, renewing the water as it evaporates, whereby there is obtained from plant-fibrin a black, from mucedin a slightly coloured liquid. This liquid is supersaturated with milk of lime, filtered, and concentrated; the dissolved lime is removed by oxalic acid, the sulphuric acid by carbonate of lead; and the solution is freed from lead by sulphuretted hydrogen, and concentrated. It then yields, if plant-fibrin has been used, a crystalline mixture of tyrosine, leucine, and glutamic acid, which may be separated by recrystallisation and treatment with warm alcohol of 30 p. c., the leucine then dissolving, while the glutamic acid remains behind.

2. Legumin or conglutin is boiled with dilute sulphuric acid, whereby knobby crystalline masses are obtained, consisting of glutamic acid mixed with optically active aspartic acid. On repeatedly boiling these masses with spirit of 50—60° p. c., the greater part of the aspartic acid remains undissolved, and an additional quantity of that acid separates from the hot alcoholic solution, while the glutamic acid remains in the mother-liquors, and may be obtained in crystals by distillation and concentration over oil of vitriol.

Properties. Shining, transparent, colourless crystals, which, according to Werther, are distorted rhombic octohedrons. Melts at about 140°, with some loss of water, but without decomposition. Has an acid taste and reaction. Dextrorotatory; for the line D, $[\alpha] = 34{\cdot}7°$.

	Crystals.		Ritthausen. *mean.*
10 C	60	40·81	41·1
N	14	9·52	9·4
9 H	9	6·12	6·3
8 O	64	43·55	43·2
$C^{10}NH^9O^8$	147	100·00	100·0

Decomposes when heated, emitting the odour of burnt horn, giving off an alkaline oil, and becoming carbonised. With *nitrous acid* the aqueous acid gives off nitrogen, and forms *glutaric acid*, $C^{10}H^8O^{10}$, an amorphous optically inactive acid, whose lead-salt, $C^{10}H^6Pb^2O^{10}$ + aq., contains 43·97 p. c. C., 4·47 H., and 51·56 O.

Glutamic acid dissolves in 100 pts. of water at 16°. It decomposes carbonates, with evolution of carbonic acid. It is bibasic. The *potash salt* crystallises with difficulty from alcohol in tufts of needles. The glutamates of the *alkaline earths* are amorphous, and very soluble in water and alcohol.—The *acid baryta salt* contains at 100°, 31·4 p.c. barium, agreeing with the formula $C^{10}NH^8BaO^8$ (calc. 31·9 p. c.).

The *neutral copper salt* obtained by boiling the acid with cupric hydrate, separates from aqueous solution in well defined deep-blue crystals, very much like those of aspartic acid; after drying in the air, they give off 29·70 p. c. water at 140° (calc. for 5HO = 30·42 p. c.).

	Dried at 140°.		Ritthausen.		*Air-dried.*		Ritthausen.
10 C	60·0	28·76	28·33	10 C	60 0	23·66	23·33
N	14·0	6·71		N	14·0	5·52	
7 H	7·0	3·36	3·90	12 H	12·0	4·73	4·69
2 Cu	63·6	30·49	29·70	2 Cu	63·6	25·08	24·75
8 O	64·0	30·68		13 O	104·0	41·01	
$C^{10}NH^7Cu^2O^8$	208·6	100·00		+ 5 aq.	253·6	100·00	

Glutamate of copper dissolves without alteration in warm nitric acid, but crystallises from the solution in very fine prisms on adding potash or soda till a deep blue colour is produced. When on the other hand a moderately concentrated and still hot solution is mixed with such a quantity of alkali as to leave a slight acid reaction, and stirred with a glass rod, small prisms soon separate, which have a dull, light blue colour when lying over one another, and are no longer soluble in boiling water. In the air-dried state they contain 25·46 p. c. copper, and when dried at 150°, give off 15·21 p. c. water, agreeing nearly with the formula $C^{10}NH^7CuO^8$ + 4HO, which requires 25·94 p. c. copper and 14·73 water.

Lead-salts do not precipitate glutamic acid, even on addition of ammonia.

The *silver-salt*, $C^{10}NHAgO^8$ is indistinctly crystalline, and contains 42·05 p. c. silver (calc. 42·5 p. c.).

Glutamic acid dissolves at 15° in 302 pts. *alcohol* of 32 p. c., in 1500 pts. alcohol of 80 p. c., and is insoluble in absolute alcohol and in

Gluten-casein.

RITTHAUSEN. *Survey of his researches on Wheat-gluten:*

1. *J. pr. Chem.* 85, 193; 86, 257; *Chem. Centr.* 1862, 725 and 728; *Jahresb.* 1862, 519 (decomposition of wheat-gluten).
2. *J. pr. Chem.* 88, 141; *Chem. Centr.* 1863, 501; *Jahresb.* 1863, 618 (plant-gelatin).
3. *J. pr. Chem.* 91, 296; *Chem. Centr.* 1864, 727; *Jahresb.* 1864, 625 (Decomposition of Wheat-gluten, Paracasein, Plant-fibrin, Mucedin).
4. *J. pr. Chem.* 99, 462; *Chem. Centr.* 1867, 271; *Jahresb.* 1866, 719 (Nomenclature).
5. *J. pr. Chem.* 99, 454; *Chem. Centr.* 1867, 273; *Jahresb.* 1866, 719 (Glutamic acid from Gluten).

Glutencasein, Paracasein.—On Plant-casein, see p. 425; also under Gluten.

Fresh, well-washed wheat-gluten is treated with cold aqueous potash-ley containing 0·1 to 0·15 p. c. potash-hydrate, a quantity of the solution containing 3 or 4 grms. of the hydrate being used to every 100 grms. of gluten; and the solution, after standing for several days at 4° to 8°, is poured off from the remains of the husks and the undissolved starch, and precipitated with a slight excess of acetic acid. The gluten thus purified is exhausted successively with cold alcohol of 60 to 80 p. c. with absolute alcohol and with ether, whereupon gluten-casein remains undissolved, while gluten-fibrin, mucedin, and vegetable gelatin remain in solution.

a. The *gluten-casein* is purified by solution in water containing potash, precipitating the filtrate with acetic acid, and washing with water and alcohol.

b. The united alcoholic extracts distilled down to one-half, deposit on cooling the *gluten-fibrin*, which is freed from gelatin, mucedin, and a little fat by absolute alcohol, and then washed with ether. The remaining substance is dried, and dissolved in a little hot alcohol of 60 p. c.; the flocks which separate on cooling are again dissolved in alcohol; the flocks of gluten-casein which first separate are removed; and the somewhat concentrated filtrate is cooled to a low temperature, whereupon after some days it deposits gluten-fibrin. This substance is to be further purified by repeated solution in alcohol of 70 p. c.

c. After separation of the gluten-fibrin, there remain in solution mucedin and vegetable gelatin, together with a small quantity of gluten-fibrin. The greater part of the alcohol is evaporated, and the remaining liquid is left to cool, whereupon a mixture of the three substances is deposited; the precipitate is dehydrated by covering it with strong alcohol, freed from fat by ether, and dissolved in alcohol of 65 p. c.; and the resulting solution is left to cool.—From the filtrate absolute alcohol throws down flocks of *mucedin*, which is purified by repeated solution and precipitation. The solution retains *vegetable gelatin* (Ritthausen).

Properties. White or grey, loose earthy mass. When imperfectly dehydrated, or simply left to dry in the air, it is horny and brownish-yellow. Nearly free from ash.

Contains at 130—135°, on the average, 51·0 p. c. C., 16·1 N., 6·7 H., 0·8 S., and 25·4 O.

Insoluble in *water*, either cold or boiling, and converted by prolonged boiling with water into an insoluble modification.—Dissolves partially in *nitric acid* of sp. gr. 1·2, with evolution of red vapours.—Dissolves sparingly in aqueous *ammonia*, and becomes insoluble therein on warming.—Dissolves easily with brownish-yellow colour, in very dilute aqueous *potash*, and from this solution metallic salts throw down bulky flocks. *Cupric sulphate* added to the alkaline solution, forms a blue precipitate, and with excess of potash, a fine violet solution.—Dissolves sparingly in cold dilute *acetic acid* and in cold *alcohol;* on warming either of these liquids, part of the gluten-casein becomes insoluble, while another part dissolves and separates on cooling from the alcoholic, but not from the acetic solution, as a curdy-flocculent mass. Dissolves more readily in alcohol containing acetic acid, and is precipitated therefrom by alkalis.

More recently (*J. pr. Chem.* 103, 216) Ritthausen gives the following characters of gluten-casein, as serving to distinguish it from legumin:—1. It is richer in sulphur. 2. It is more soluble in acetic acid. 3. When boiled with sulphuric acid, it yields, besides other known products, glutamic acid (p. 437), which latter, however, Ritthausen afterwards also obtained from legumin (*J. pr. Chem.* 107, 218).

Rye-casein.—Rye yields gluten-casein and mucedin, but no gluten-fibrin or plant-gelatin.—Fine rye-flour is macerated with a large quantity of water containing 0·2 p. c. potash hydrate; the same treatment is repeated after 24 hours, at 1°—2°; the whole is left to itself for three or four days; the clear liquid obtained by decantation or filtration is slightly supersaturated with acetic acid; and the precipitated greyish-white flocks, after successive treatment with absolute alcohol, to dehydration, then with ether, and once more with absolute alcohol, are quickly dried in a vacuum over oil of vitriol.—Yellow-grey, loose mass, having an earthy fracture; permanent in the air when dry.

After deduction of 0·7 p. c. ash, it contains, at 125—130°, on the average, 51·23 p. c. C., 15·96 N., 6·70 H., 1·04 S., and 25·67 O., and is therefore composed like gluten-casein, excepting that it contains a larger proportion of sulphur.

Rye-casein moistened with water, becomes dark-coloured on exposure to the *air*, and changes to a brown horny mass.—Swells up in cold or warm *water*, without dissolving.—Dissolves incompletely in boiling *nitric acid* of sp. gr. 1·2, with separation of yellowish-white flocks, the yellow solution becoming darker when supersaturated with potash.—Dissolves in *oil of vitriol* diluted with an equal volume of water, with deep brown colour at the boiling heat.—Swells up in strong *hydrochloric acid* to black-brown gummy flocks, and dissolves gradually to a brown liquid precipitable by water.—Dissolves in cold aqueous *potash*, *soda* (or *ammonia*) of 0·1 to 0·2 p. c., forming a brown-yellow liquid. The solution is precipitated by acids in the cold, by *sal-ammoniac*, by *lime-salts*, or by *sulphate of magnesia* mixed with sal-ammoniac, only at the boiling heat, and then yields a curdy white precipitate; it is not precipitated by *ferro-* or *ferri-cyanide of potassium.*—In very dilute *acetic acid*, rye-casein swells up to brown flocks, which then dissolve, especially on boiling; the resulting solution is precipitated by ammonia and the fixed alkalis, also by ferrocyanide and ferricyanide of potassium. By prolonged boiling with water, rye-casein becomes insoluble in acids and in alkalis. It is insoluble in *alcohol* (Ritthausen, *J. pr. Chem.* 99, 439).

To this head belong probably a *plant-fibrin* containing 53·59 p. c. C., 15·81 N., 7·49 H., 23·11 O. and S., which Scherer (*Ann. Pharm.* 40, 7) obtained by boiling rye-flour with dilute sulphuric acid, dissolving the residue in very weak potash-ley, precipitating with acetic acid, and boiling the precipitate with alcohol and ether. In this or a similarly prepared product from rye, Verdeil (*Ann. Pharm.* 58, 317) found 0·98 p. c. sulphur.

From oil-cake of *rape-seed* previously freed from fat, Ritthausen (*J. pr. Chem.* 103, 206) obtained a proteide probably identical with gluten-casein, which, after deduction of 2·09 p. c. ash, contained 50·36 p. c. C., 16·28 N., 6·79 H., 1·02 S., and 25·55 O.

Gluten-fibrin.

RITTHAUSEN. *J. pr. Chem.* 91, 296.

On Plant-fibrin, see page 423, and under Gluten.

Preparation. p. 439.

Properties. Separates from the alcoholic solution as a tough brown-yellow mass, which, when immersed in absolute alcohol, becomes yellowish-white and opaque, and hardens. When dry, it forms hard, brittle, horny plates, which, if the drying has been performed otherwise than in a vacuum, are obtained in the insoluble modification.

Contains, on the average, at 130°—135°, together with traces of ash, 54·31 p. c. C., 16 89 N., 7·18 H., and 20·61 O.

Insoluble in water, and converted by prolonged contact with cold water, or in a shorter time by boiling with water, into a translucent jelly, insoluble in alcohol, acetic acid, and potash-ley. — Swells up in *ammonia-water* to a transparent jelly, without dissolving. — Dissolves easily in cold very dilute aqueous alkali, the solution being precipitated by acids and by metallic salts. — Dissolves easily in dilute *acetic acid,* forming a brownish-yellow solution precipitable by alkalis, gradually also in cold aqueous *tartaric acid.* — Dissolves completely in a large quantity of cold alcohol, the solution during concentration forming on the surface a soft, transparent film, which is continually renewed; the solution in hot alcohol of 30—70° p. c., deposits a large quantity on cooling.

Maize-fibrin.

GORHAM. *Journal of Science,* 11, 206; *Berzel. Jahresb.* 2, 124.
STEPF. *J. pr. Chem.* 76, 88; *Chem. Centr.* 1859, 626; *Jahresb.* 1859, 592.
RITTHAUSEN. *J. pr. Chem.* 106, 471.

Gorham's *Zein.* Forms the only proteide of maize-seed, which is soluble in alcohol.

Preparation. Maize-flour is exhausted by treating it three times with alcohol of 80 p. c., which is made to act upon it at 40°—50°, or at the boiling heat, each time for an hour; the liquid is distilled till the tincture begins to show turbidity, then left to cool; and the mixture of fat and maize-fibrin which separates is collected. It is freed from fat by successive treatment with absolute alcohol and ether, or better by pouring the solution in alcohol of 90 p. c., concentrated as much as possible, into a large quantity of absolute alcohol, and repeatedly kneading the tough gummy mass with fresh quantities of absolute alcohol. Having been thus deprived of its ductility, it is cut up, repeatedly treated with ether, and then again with absolute alcohol, and dried over oil of vitriol.

Maize-fibrin thus prepared cannot be resolved into separate parts, either by solution in alcohol of 80 p. c. and partial precipitation with absolute alcohol, or by solution in aqueous potash of 0·1 p. c., and precipitation with acetic acid; or, lastly, by treatment with acetic acid and precipitation with potash. But if in these operations the alcoholic solution has been too strongly heated, part of the maize-fibrin is converted into a modification not soluble in alcohol of any degree of concentration, and presenting the appearance of a transparent jelly. A second insoluble modification is obtained by pouring the concentrated alcoholic solution of maize-fibrin into a large quantity of ether; it dissolves in alcohol, but not in aqueous potash (Ritthausen).

Properties. Yellowish, very tenacious, horny mass, brittle in the larger lumps, but not friable. Free from ash.

	Ritthausen. *mean, at* 140°.	
	a.	*b.*
C	54·66	54·71
N	15·50	15·53
H	7·45	7·60
S	0·69	
O	21·70	
	100·00	

a is maize-fibrin, soluble; *b*, insoluble in alkaline water. The nitrogenous substance extractable from maize-flour by boiling alcohol, reacts like a mixture of plant-casein and plant-gelatin, and contains 15·6 p. c. nitrogen (v. Bibra).

Maize-fibrin is insoluble in water, whether cold or at the boiling heat, but is transformed by prolonged boiling with water, aqueous alcohol, or dilute acids, into the modification insoluble in dilute acids and alkalis, which then separates from the alcoholic solution as a transparent jelly, becomes horny after drying, and swells up again to a jelly in strong acetic acid without dissolving (Ritthausen).

Dissolves in *nitric acid* of sp. gr. 1·2, decomposing on prolonged boiling. When boiled with *oil of vitriol* diluted with an equal volume of water, it dissolves to a light yellow-brown liquid, which is not precipitated by water. Oil of vitriol at the heat of the water-bath forms with fibrin a colourless solution, partially precipitable by water, and assuming a fine violet colour when mixed, after dilution, with cupric sulphate and potash. Dissolves slowly with faint brown colour in strong *hydrochloric acid*, and is precipitated from the solution by water n).

Dissolves sparingly in *ammonia-water*, either dilute or concentrated. Dissolves easily, more slowly after drying, in aqueous *potash* of 0·1 p. c., not in *lime-water*, *baryta-water*, or in aqueous solutions of the *alkaline carbonates* or *phosphates*. The alkaline solution is precipitated by acids and by metallic salts (Ritthausen).

Dissolves slowly in the cold, more quickly when heated, in strong *acetic acid*, forming a yellow liquid, which becomes milky when mixed with water, and is precipitated by ammonia or potash. Modified maize-fibrin swells up in glacial acetic acid to a transparent jelly without dissolving. Dilute acetic acid dissolves a small quantity of maize-fibrin, forming a turbid liquid.

From the solution in acetic acid, cupric acetate, neutral lead acetate, potassium ferrocyanide, and many other metallic salts, throw down white cohering flocks, apparently consisting of unaltered maize-fibrin.

Very dilute *alcohol* dissolves only traces of maize-fibrin in the cold, a somewhat larger quantity when heated, and renders the rest insoluble. Boiling alcohol of 50—60° p. c. forms a clear solution, which on cooling deposits the whole of the maize-fibrin as a tough viscid mass. Alcohol of 70—90° p. c. dissolves maize-fibrin even in the cold, and with greater facility the stronger it is; when moderately heated, it quickly dissolves maize-fibrin to a yellow liquid, which remains clear when quite cold, even if it has been concentrated to an oily consistence by distilling off the alcohol.

This is true, especially for alcohol of 80—90 p. c., whereas weaker alcohol, after it has become watery by partial distillation, deposits the maize-fibrin as a jelly on cooling. When the solution, concentrated as above mentioned to an oily consistence, is left to evaporate in a thin layer on a glass plate, the maize-fibrin remains in transparent flexible films (Ritthausen).

Wheat-mucedin.

RITTHAUSEN. *J. pr. Chem.* 91, 296.

Mucin. Mucedin. Compare page 423.

Preparation, p. 439.

Properties. Mucedin, which is gummy when recently separated, forms, after drying in a vacuum, slightly coherent lumps, and after drying in the air, a transparent, brittle, light yellow mass.

Contains at 130°, 54·11 p. c. C., 16·33 N., 6·90 H., 0·88 S., and 21·48 O.

Recently prepared mucedin, stirred up with cold *water*, diffuses itself, and forms a turbid gummy liquid, without dissolving to any considerable extent. Boiling water forms a milk, which, after standing for a week, deposits tenacious flocks only partially soluble in alcohol and acetic acid. Dissolves easily in cold very dilute *acids*, and is precipitated by alkalis from the acetic solution in gummy flocks; easily also in very dilute aqueous *alkalis*, *lime-water*, and *baryta-water*, the solutions being precipitated by acids and by metallic salts.—By prolonged boiling with moderately dilute sulphuric acid, more than 30 p. c. of the mucedin is obtained as glutamic acid, together with small quantities of leucine, but no tyrosine (Ritthausen, *J. pr. Chem.* 99, 454).

Alcohol of 60 to 70 p. c. dissolves mucedin easily and completely, the solution not becoming turbid on cooling, but being precipitated in flocks by alcohol of 90 to 95 p. c.; alcohol of less than 60 p. c. dissolves mucedin with aid of heat, and deposits it on cooling, in larger quantity the weaker it is.

Rye-mucedin.—Fine rye-flour is boiled five times with about an equal weight of alcohol of 80 p. c., the liquid being strained each time at the boiling heat and then left to cool. The precipitate which settles after 24 hours from the brown-red liquid is treated successively with absolute alcohol and with ether, dissolved in boiling alcohol of 80 p. c., the solution depositing mucedin on cooling, and a larger quantity when the alcohol is distilled off. It is dehydrated by immersion in absolute alcohol, dried in a vacuum over oil of vitriol, dissolved in acetic acid, and mixed by drops with potash-ley, whereby part of the mucedin is precipitated, together with the whole of the gum. The purer mucedin is precipitated from the filtrate by neutralisation with potash (Ritthausen).

Rye-mucedin resembles the similarly named substance from wheat, and approximates to it in composition. Contains, after drying at 125°—130°, after deduction of 0·43 p. c. ash, 53·61 p. c. C., 16·84 N., 6·79 H., 0·50 S., and 22·26 O. (Ritthausen).

Rye-mucedin dissolves to a certain extent in hot *water*; if the quantity of water is insufficient for complete dissolution, the residue becomes suspended, forming a milky liquid, which forms a deposit on cooling.

By prolonged boiling with water it becomes insoluble in acids and in alkalis.—Dissolves in hot *nitric acid* of sp. gr. 1·2, with slight evolution of red vapours, the solution becoming turbid on cooling.—*Oil of vitriol* diluted with an equal volume of water forms, after boiling for a short time, a clear reddish solution; if the solution contains gum, or a similar substance, the solution is dark brown, and rendered turbid by black flocks. By prolonged boiling the same products are obtained as from wheat mucedin, especially a large quantity of glutamic acid. The solution slightly acidulated with acetic acid is precipitated in white flocks by *mercurous nitrate*, acquires a fine violet-red colour when heated after addition of a small quantity of *cupric sulphate* and *potash*, blue in presence of sugar or gum.—Dissolves slightly in cold *alcohol* of 30 p. c., more abundantly in stronger alcohol, especially of 60 to 85 p. c., the solutions depositing mucedin again only when strongly concentrated and cooled to a low temperature. From these solutions it is precipitated by absolute alcohol, either as a translucent film, or from a non-saturated solution as a reddish-yellow translucent jelly, becoming yellowish-grey and opaque when left immersed in absolute alcohol (Ritthausen).

As Ritthausen's mucedin is the only constituent of rye-flour that is soluble in alcohol, the *plant-gelatin from rye*, examined by Helot (*Ann. Pharm.* 45, 198), probably belongs to this place. It is obtained by exhausting rye-flour with alcohol, distilling off the alcohol, and exhausting the yellow-brown glutinous residue with ether and alcohol.—After drying it is dark brown, horny, and shining, has a faint acid reaction, contains 0·47 p. c. ash, and after deduction thereof 55·51 p. c.

C., 15·83 N., 7·97 H. — Insoluble in cold, slightly soluble in boiling water; dissolves almost entirely in hot dilute acids and in hot acetic acid, the solutions depositing flocks on cooling, and being precipitable by alkalis. Dissolves with difficulty in cold, more easily in hot aqueous *ammonia*, in aqueous *potash*, especially when heated, with copious evolution of ammonia, and formation of potassium sulphide. Dissolves easily in boiling *alcohol*, and is precipitated by water. — On Plant-albumin from rye examined by Liebig and Jones, see p. 427.

Plant-gelatin.

BERZELIUS. *Pogg. Ann.* 10, 248. *Berzel. Jahresbr.* 7, 231. — Taddei, *Brugn. Giorn.* 12, 360; *N. Tr.* 4, 2, 154. Schw. 29, 514.
BOUSSINGAULT. *Ann. Chim. Phys.* 63, 225; 65, 301; *Berzel. Jahresb.* 18, 327.
LIEBIG. *Ann. Pharm.* 39, 142. JONES. *Ann. Pharm.* 40, 66.
DUMAS & CAHOURS. *N. Ann. Chim. Phys.* 6, 418.
v. BIBRA. *Die Getreidearten und das Brod.* Nürnberg, 1860, 152.
GÜNSBERG. *Wien. Acad. Ber.* 44, 429; *J. pr. Chem.* 85, 213; *Chem. Centr.* 1862, 161; *Jahresber.* 1862, 517.
RITTHAUSEN. *J. pr. Chem.* 85, 193; 86, 257; *Chem. Centr.* 1862, 725; *Jahresber.* 1862, 519. — *J. pr. Chem.* 88, 141; *Chem. Centr.* 1863, 401; *Jahresber.* 1863, 418.

Gliadin. Glutin. A constituent of wheat-gluten, perhaps also of oats (see below).

Preparation. Obtained together with the other constituents of wheat-gluten (p. 439).

Or recently prepared gluten is immersed for 24 hours in cold alcohol of 80·85 p. c.; the solution, containing plant-gelatin together with gluten-fibrin and fat, is evaporated to dryness, whereby the gluten-fibrin becomes partly insoluble; and the residue is warmed with very dilute acetic acid. From the liquid filtered from the undissolved gluten-fibrin, ammonia added in separate portions first throws down gelatin containing fibrin, as a gelatinous flocculent mass, then purer gelatin as a clear colourless varnish. It is dehydrated by immersion in absolute alcohol, and dried over oil of vitriol in a vacuum, finally at 130° (Ritthausen).

When gluten is exhausted with boiling alcohol, first of 80—85 p. c. afterwards of 75 p. c., the tinctures, after distillation to one-half, deposit flocks of gluten-fibrin containing fat, then, after complete cooling, first, gelatin containing fibrin, then purer gelatin as a transparent ropy mass, a portion also remaining in solution together with dextrin and gum (Ritthausen).

Dumas & Cahours exhaust gluten with boiling alcohol, remove the deposit which separates on cooling, and concentrate, the liquid then coagulating in consequence of the separation of plant-gelatin. The gelatin is purified by exhaustion with ether, alcohol, and water. — v. Bibra proceeds in a similar manner.

The plant-gelatin analysed by Jones was prepared by Liebig, apparently (according to *Ann. Pharm.* 39, 147) by exhausting wheat-gluten with alcohol, evaporating, washing the residue with hot water, dissolving in acetic acid, and precipitating the filtrate with ammonia, whereupon, before the acetic acid is neutralised, there falls down a white, non-glutinous but ropy mass, which must be treated with ether to remove a substance resembling bird-lime. — On plant-albumin from gelatin, see p. 452.

Günsberg boils wheat-gluten for some hours with water, strains the greenish-yellow decoction, and concentrates, whereupon films of starch appear upon the surface, and after these have been separated and the liquid cooled, the remainder separates into a gelatinous deposit of gluten-gelatin and a milky turbid liquid. The deposit dissolved in cold alcohol of 50 p. c. separates out again on concentration, and on redissolving it in boiling water, and evaporating the solution, it is obtained as a brown transparent mass, which has partly become insoluble in boiling water and in weak spirit. Compare p. 447.

Properties. Plant-gelatin is obtained by evaporation of its alcoholic solution in amorphous, transparent, yellowish-white, brittle laminæ; by evaporation of its aqueous solution in a vacuum, as a blistered mass. But if the moist gelatin be immersed for 24 hours in a large quantity of absolute alcohol and kneaded from time to time, the alcohol which has become milky and watery being replaced by fresh alcohol, the mass, which is gummy at first, becomes opaque, and then dries up in a vacuum to an earthy, lustreless, easily friable mass (Ritthausen).

	Jones.	Dumas & Cahours. *at* 140°.	v. Bibra.	Günsberg. *at* 130°.	Rittshausen. *at* 130°.
C	54·47	53·27	53·56	52·73	52·60
N	15·98	15·94	15·56	17·70	18·06
H	7·42	7·17	7·12	6·81	7·00
S	22·13	23·62	0·88	22·76	0·85
O			22·88		21·49
	100·00	100·00	100·00	100·00	100·00
Ash		0·70	3·90	0·41	0·26

Günsberg's plant-gelatin was free from sulphur, in consequence, as Ritthausen supposes, of previous decomposition. — The body analysed by Mulder as plant-gelatin appears to belong to plant-fibrin (p. 451).

The *gelatin of oats*, purified by repeated solution in alcohol of 60 p. c., and precipitation with absolute alcohol, contains at 130°, 52·49 p. c. C., 17·71 N., 7·65 H., 1·66 S., and 20·39 O, therefore twice as much sulphur as that of wheat, the characters of which it exhibits in other respects (Kreusler, *J. pr. Chem.* 107, 17).

Decompositions and Combinations. 1. Melts *when heated*, and decomposes with strong intumescence, leaving a difficultly combustible charcoal. — 2. Moist vegetable gelatin becomes dark-coloured on exposure to the air, or when repeatedly evaporated by heat (Ritthausen).

3. Dried plant-gelatin swells up in cold *water* to a soft whitish mass, and dissolves slightly, forming a turbid frothy liquid. — With boiling water it forms a clear solution, which becomes milky on cooling; but when it is repeatedly boiled with quantities of water not sufficient to dissolve it, there remains a transparent, gelatinous, very glutinous residue, containing less nitrogen and more sulphur than the plant-

gelatin employed. The solution prepared at the boiling heat also leaves, on evaporation to dryness, a portion of the gelatin converted into the insoluble modification. — 4. The gluten-gelatin of Günsberg dissolves very easily in water containing traces of *acid*, without neutralising the acid; on further addition of acid, the solution becomes turbid and afterwards clear again (Günsberg).

With boiling concentrated *hydrochloric acid*, with *nitric acid*, with *oil of vitriol* and *sugar*, and with *cupric sulphate* and *potash*, plant-gelatin exhibits the same reactions as other proteides.

5. When *chlorine gas* is passed into a hot aqueous solution of plant-gelatin, the gas-bubbles become surrounded with a white film, then rise, and form a floating coherent mass, whilst a glutinous substance separates at the bottom. Both compounds smell strongly of chlorine; the first dries up to a white friable mass, the second to a hard transparent glue (Günsberg).

6. Water containing 0·2 p.c. potash (or soda) dissolves plant-gelatin on prolonged standing, forming a clear yellow alkaline liquid, 1 pt. of potash being capable of taking up 22 pts. or more of plant-gelatin. It is not till the solution is heated, that sulphide of potassium can be detected in it by nitro-prusside of sodium. — 7. Dissolves in aqueous *ammonia* less easily than in the fixed alkalis, forming a turbid liquid, also in *lime-water* and *baryta-water* (Ritthausen). Insoluble in aqueous *carbonate* or *nitrate of potash* (v. Bibra).

8. With *iodine-solution*, *metallic salts*, and *tannic acid*, solutions of plant-gelatin exhibit the following reactions. — *a.* The cold aqueous solution is clouded by *zinc sulphate*, *basic lead acetate*, *silver nitrate*, *mercurous nitrate*, *mercuric chloride* and *tannic acid*. — With *ferric sulphate* mixed with sufficient ammonia to produce a blood-red colour, it forms an orange-coloured or brown precipitate, which contracts to an elastic mass. — *b.* The solution in alkaline water forms with the same metallic salts, curdy flocculent precipitates, and moreover precipitates *ferric chloride* yellow-brown, *cupric sulphate* blue, *platinic chloride* yellow. It precipitates aqueous or alcoholic *iodine*, after addition of potassium iodide, in brown flocks. It is clouded by soluble *carbonates*, *lime-salts*, *alum*, *neutral lead-acetate*, and *potassium-ferrocyanide*, and afterwards becomes clear, with separation of unaltered gelatin. — *c.* From the solution of plant-gelatin in acetic acid, most metallic salts precipitate unaltered gelatin; *mercurous nitrate* immediately throws down curdy flocks; so likewise does *mercuric chloride* after addition of potash. — *d.* The alcoholic solution is precipitated only by *mercurous nitrate*; clouded by *ferric chloride* and *mercuric chloride* (Ritthausen).

9. Plant-gelatin dissolves easily and abundantly in *acetic acid*, either cold or warm, dilute or concentrated; the solution is not precipitated by alcohol, but alkalis and alkaline carbonates precipitate it completely long before it has become neutral (Ritthausen; Liebig). Aqueous *tartaric acid* dissolves plant-gelatin on boiling; in aqueous *oxalic acid* it is almost insoluble (Ritthausen).

10. Dissolves abundantly in alcohol of 40 to 80 p.c.; the solution is rendered milky by a large quantity of water and by absolute alcohol, precipitated in flocks by ether. The turbidity produced by water col-

lects into a clear varnish; that produced by alcohol into an opaque, apparently fine-grained coherent film (Ritthausen).

From solutions of plant-gelatin in aqueous acids, *dextrin* throws down a precipitate, which does not dissolve either in a larger quantity of acid, or on further addition of dextrin (Günsberg, *Wien. Acad. Ber.* 45, 643; *Chem. Centr.* 1863, 460; *Jahresb.* 1863, 571).

Appendix to the Proteides of Wheat.

Gluten.

On the preparation of gluten, see p. 422. — The separation is easier when the stiff paste formed of wheat-flour and water is left to itself for a quarter of an hour (v. Bibra).

Of the proteides of wheat which are insoluble in water, a part only is obtained as gluten, the remainder being diffused in the starch-water, and deposited for the most part in the lower layers of the starch as a dark-coloured mass (v. Bibra).

According to Ritthausen, gluten contains 12 to 16 p. c. starch, husks and fat, and 16 to 20 p. c. gluten-casein, the rest consisting of gluten-fibrin, mucedin and plant-gelatin in about equal parts. Fresh gluten contains about 70 p. c. water, but shrinks after some time and extrudes some of the water; in the dry state it contains 70 to 71 p. c. plant-fibrin, between 3·85 and 9·35 p. c. plant-casein, 7·54 to 19·56 plant-gelatin, and 4·61 to 8·15 p. c. fat (v. Bibra).

In the moist state, gluten forms a light yellow, tough, elastic adhesive mass, which, when prepared from fine flour, is without taste or smell, and may be spread out into sheets as thin as paper, and nearly as large as the hand (v. Bibra). — After boiling with alcohol it is whitish-grey and hard (Ritthausen). Dried gluten is brown, translucent on the edges, and brittle, and may be kept for a long time if excluded from moisture (v. Bibra). In hydrochloric acid solution it is optically lævorotatory (Bouchardat).

Gluten prepared by Beccaria's process.

	Marcet. (*Ann. Chim. Phys.*, 36, 27.)	Boussingault. (*Ann. Chim. Phys.*, 65, 301).
C	54·65	52·54
N.	14·50	15·00
H.	7·80	7·50
O and S	23·05	24·96
	100·00	100·00

Boussingault's gluten contained 1·3 p. c. ash. See its composition, according to Kekulé (Liebig's *Chem. Briefe.* 592; *Jahresber.* 1851, 715). In crude gluten freed as far as possible from fat, Ritthausen found 12·7 p. c. nitrogen.

Moist gluten coagulates when *heated*, and becomes for the most part insoluble in potash-ley, acids, and alcohol, even when merely dried by heat (Ritthausen).

Dried gluten takes up water again but slowly, and does not com- recover its extensibility (v. Bibra). Boiling water abstracts plant- and other substances from moist gluten, Günsberg (p. 424), but alters its constituents (Ritthausen). By heating gluten with 6 pts. of water to 200°—220°, a turbid brown alkaline liquid is obtained, from which acids throw down a yellow precipitate (Gmelin. — Barral, *Compt. rend.* 56, 1118; *Jahresber.* 1863, 762). — Moist gluten soon gives off carbonic acid, and deliquesces to a varnish-like mass, almost wholly soluble in alcohol, emitting at the same time an odour of putrefaction and of hydrosulphuric acid (v. Bibra). In a vessel filled with water and closed, gluten does not alter; but in a cold aqueous extract of malt it swells up, gives off gas, and dissolves to an acid liquid, which is precipitated by boiling, and also, after this precipitate has been filtered off, by mercuric chloride (Mulder, *Scheik. Verhandl. en Onderzoek.* 130; *Jahresb.* 1858, 586).

Fresh gluten not coagulated by heat, dissolves in dilute *phosphoric acid.* It dissolves in cold fuming *sulphuric acid* with reddish black-brown colour (Link, *Schw.* 14, 292): hot *oil of vitriol* colours it violet to black, eliminates combustible gas, and forms acetic acid and ammonia (Fourcroy). By prolonged boiling with moderately dilute sulphuric acid, it yields tyrosine, leucine, glutamic acid (p. 437), aspartic acid, and a product resembling leucine, containing 47·03 p. c. C., 13·46 N., 7·43 H. (Ritthausen). — When fresh gluten is added to *oil of vitriol* as long as it dissolves without blackening, and the solution after dilution with water is distilled, with addition of *peroxide of manganese,* there pass over, with the vapour of water, the following volatile acids: benzoic, formic, acetic, propionic, butyric, and valeric, together with the aldehydes of acetic, butyric, valeric, and benzoic acids; the residue supersaturated with lime, gives off ammonia smelling of volatile bases (Keller, *Ann. Pharm.* 72, 14). — Warm *nitric acid* colours fresh gluten yellow, and decomposes it, with formation of oxalic acid, sulphuric acid, ammonia, sebaceous matter, artificial bitter, and other products. — Gluten dissolves in hot *hydrochloric acid* with brown colour, forming ammonia after some time (Poulletier de la Salle). — The bluish-grey solution in strong hydrochloric acid deposits grey flocks on addition of water, and forms with the colourless solution of starch in fuming hydrochloric acid, a purple-red liquid, becoming yellow on addition of alkalis (Vauquelin). Aqueous hydrochloric acid containing 0·05 to 0·2 p. c. of the gaseous acid, dissolves gluten, forming a solution which becomes turbid on boiling, gives with acids precipitates which dissolve in excess of the precipitant, and in general is precipitated by all substances which precipitate solutions of albumin. — (Bouchardat, *Compt. rend.* 14, 962). — In *chlorine-water* gluten coagulates to yellowish-white flocks containing chlorine (Fourcroy & Vauquelin).

In aqueous *ammonia* gluten swells up and falls to pieces without dissolving (Lenk). Coagulated gluten also does not dissolve in ammonia or *carbonate of ammonia.* Gluten precipitated from acid solutions by carbonate of ammonia becomes transparent and gummy when washed with water, and partly dissolves; the portion precipitated from the alkaline solution by carbonate of ammonia dissolves in a considerable quantity of water (Berzelius). — Aqueous *potash* and *soda* dissolve gluten in the fresh state, or when it has been dried without application of heat; from the solution diluted till it contains only 0·1 to 0·2 p. c. and kept cold, the gluten is precipitated by acids without alteration (Ritthausen). — Sulphuric, hydrochloric, and nitric acid precipitate the alkaline solution immediately; phosphoric and acetic acids form, at the point of exact neutralisation, a precipitate which dissolves in a larger quantity of acid, forming a solution which may be evaporated without coagulation (Taddei). — Hot aqueous alkalis dissolve gluten with evolution of ammonia (Fourcroy).

Gluten dissolved in aqueous potash, precipitates the salts of the *earths* and *heavy metals*. — *Cuprate of ammonia* dissolves one part of the gluten and causes another portion to swell up, but this latter portion does not dissolve even in a larger quantity of cuprate of ammonia. The solution is precipitable by hydrochloric acid (v. Bibra). — Fresh gluten hardens with *mercuric oxide* or *chloride*, the latter being partly reduced to calomel, and becomes unputrefiable (Taddei). — On the reaction of gluten with starch, see xv, 91.

Gluten, either fresh or dried without heating, dissolves almost wholly in dilute acetic acid or aqueous tartaric acid in the cold, leaving starch, remains of husks, and fat, and forming a liquid rendered milky by fat, without appearance of decomposition. Of gluten dried by heat, a small portion only dissolves in alkalis, acids, and alcohol (Ritthausen).

Gluten is insoluble in *ether*, *volatile oils*, and *fixed oils*. Its solutions are precipitated by infusion of galls.

Alcohol acidulated with sulphuric acid takes up from gluten a large quantity of soluble matter, and the solution gives with water a precipitate (containing 15·3 p. c. nitrogen), the quantity of which amounts to only part of the dissolved substance (v. Bibra). Boiling alcohol containing 3 to 5 p. c. sulphuric acid, dissolves gluten easily and completely, with exception of the starch and husks (Fr. Schulze, *J. pr. Chem.* 16, 187). — *Alcohol acidulated with acetic acid* dissolves a small quantity of gluten in the cold, and from the hot-prepared solution part of the dissolved matter separates on cooling (v. Bibra).

Fresh gluten digested with *alcohol containing potash* dissolves almost completely, and the solution is but slightly clouded by water, in consequence of the separation of fat. The solution contains sulphide of potassium; is not precipitated by hydrochloric acid; deposits carbonate of potash free from organic matter when carbonic acid gas is passed through it; and turns brown when evaporated, even after neutralisation (v. Bibra).

When gluten is treated with cold alcohol, first of 60 and afterwards of 80 p. c., plant-gelatin, gluten-fibrin, and mucedin chiefly pass into solution, whilst gluten-casein remains undissolved. Boiling alcohol likewise partly converts the three first-named constituents of gluten into insoluble modifications, which mix with the gluten-casein. In this manner is produced the *plant-fibrin* or *vegetable fibrin* of some chemists, that is to say, the portion of gluten insoluble in boiling alcohol, consisting mainly of gluten-casein with smaller quantities of gluten-fibrin, mucedin, and plant-gelatin, which have been rendered insoluble (Ritthausen). See also p. 425.

It had previously been observed by v. Bibra, that a part of the constituent of gluten which is soluble in cold alcohol, acquires by repeated treatment with boiling alcohol the properties of plant-casein and plant-fibrin.

Analyses of Plant-fibrin.

	Scherer. *at* 100°.	Jones.	Rüling. *at* 140°.	Dumas & Cahours. *at* 140°.	v. Bibra.
C	53·02	52·82	53·64	53·23	53·57
N	15·58	15·58		16·41	15·70
H	7·22	7·02	7·17	7·01	6·95
S and O	24·18	24·58		23·35	23·78
	100·00	100·00		100·00	100·00
Ash	1·19			1·06	

Scherer (*Ann Pharm.* 39, 145 and 40, 6) dissolved wheat-gluten in water containing potash, precipitated with acetic acid, and analysed the portion of the precipitate insoluble in boiling alcohol and ether. — Jones (*Ann. Pharm.* 39, 145; 40, 65), Ruling (*Ann. Pharm.* 58, 306), and v. Bibra examined the portion of gluten insoluble in boiling alcohol; Ruling found 1·3 p. c. sulphur; v. Bibra, in fibrin from wheat, an average of 1·21 p. c.; in that from spelt, an average of 1·30 p. c. S. Mulder (*Scheik. Onderzoek.* 4, 404; *J. pr. Chem.* 44, 503), after dissolving in potash and precipitating with acetic acid, found 0·66 p. c. S. Dumas & Cahours (*N. Ann. Chim. Phys.* 6, 400) found that gluten, after thorough boiling with alcohol and ether, still contained starch; they therefore digested it with diastase at 70—80°.

Plant-fibrin, according to v. Bibra, exhibits the following properties: —It is fibrous, like animal fibrin, but loses this property by solution and re-precipitation. It is coloured brown-red to black by oil of vitriol; nitric acid colours it yellow, and partly dissolves it. Plant-fibrin dissolves partially in dilute hydrochloric acid while moist, but is insoluble after drying; dilute phosphoric, acetic, and tartaric acid also dissolve it only in the moist state. In the concentrated state these four acids likewise dissolve dried plant-fibrin, hydrochloric acid forming a blue solution, which is precipitated by water and by alkaline carbonates. — Potash-ley dissolves both fresh and dried fibrin, and decomposes it, after digestion for some time, forming metallic sulphide; the precipitate thrown down by acids from the alkaline solution dissolves in excess of the precipitant. Plant-fibrin does not dissolve in aqueous carbonates and nitrates of the alkalis, but unites in the moist state with carbonate of potash, to form a hard, opaque mass. The same hard mass is obtained by treating moist plant-fibrin with mercuric chloride (v. Bibra, *Die Getreidearten und das Brod*, Nürnberg 1860, 149).

The alcoholic solution of gluten becomes turbid as it cools, from separation of a tough glutinous mass. The body thus separated which, according to its mode of preparation, agrees most nearly with Ritthausen's gluten-fibrin, is described by Dumas & Cahours and by v. Bibra as *plant-casein*, by Mulder (*Scheik. Onderz.* 2, 154; *J. pr. Chem.* 32, 176) as plant-gelatin.

Analysis of Plant-casein.

	Dumas & Cahours. *at* 140°.	Mulder. *at* 130°.	v. Bibra.
C	53·46	53·81	54·88
N	16·04	15·71	15·71
H	7·13	7·05	7·05
S	23·37	0·60	0·70
O		22·83	21·66
	100·00	100·00	100·00

Subsequently (*Scheik. Onderz.* 4, 404; *J. pr. Chem.* 44, 503) Mulder found 0·9 to 1·0 p. c. sulphur.

The constituent of wheat-gluten which is soluble in alcohol, and is obtained as a soft glutinous mass by evaporating the alcohol and washing out the residue, deposits, when its ammoniacal solution is mixed at the boiling heat with acetic acid, a white coagulum which gives up ammonia when boiled with water containing acetic acid: *Plant-albumin from plant-gelatin.* It contains, according to Will & Varrentrapp, 53·81 p. c. C., 15·88 N., 6·98 H., and 23·43 O. (Liebig, *Ann. Pharm.* 39, 144).

The *Phytocoll* of the older chemists, *Phyteumacolla* of Brandes, is obtained from agarics, from *Lichen parietinus*, from the root-bark of *Aylanthus glandulosa*, from bitter-apples, from Spanish pepper, and from Colombo-root, and is the part of the aqueous extract of these plants which is insoluble in boiling alcohol. It is nitrogenous and dissolves in water, to a non-gelatinising liquid precipitable by many metallic salts and by infusion of galls. See Vauquelin (*Ann. Chim. Phys.* 85, 5); Braconnot (*J. Phys.* 84, 295 and 340.—*Ann. Chim. Phys.* 6, 130); Planche (*A. Tr.* 22, 2, 158); Lassaigne & Feneulle (*Ann. Chim. Phys.* 12, 358); Schröder (*Berl. Jahrb.* 1819, 67).

In *Borago officinalis* (Proust) and in other boraginaceous plants (Braconnot) there occurs a nitrogenous substance differing from gluten, the solution of which in boiling water solidifies on cooling to an imperfect jelly, and is precipitated by acids. It is also precipitated by the alkaline earths and by most salts, but tannin merely clouds it (Braconnot, *J. Phys.* 84, 274).

The *Goemin* of Blondeau occurs in the Carragheen mass of *Sphærococcus crispus*, in which, however, Mulder and C. Schmidt (xv, 210) found only vegetable mucilage. It is obtained by boiling the plant with water for several hours, precipitating the mucilage thus obtained with alcohol, redissolving the precipitate, and diluting the aqueous solution.—Translucent hard skins, neutral, swelling up in water, and soluble in aqueous alkalis. Contains 21·80 p. c. C., 21·36 N., 4·87 H., 2·51 S., and 29·46 O. (Blondeau, *Compt. rend.* 60, 860; *Krit. Zeitschr.* 8, 419).

Emulsin.

Liebig & Wöhler. *Ann. Pharm.* 22, 17; *Berzel. Jahresber.* 18, 346.
Thomson & Richardson. *Ann. Pharm.* 29, 180; *Berzel. Jahresber.* 20, 429.
Ortloff. *N. Br. Arch.* 48, 12; *Berzel. Jahresber.* 27, 397.
Bull. *Ann. Pharm.* 69, 145; *Lieb. Kopp Jahresber.* 1849, 493.

Robiquet's *Synaptase.* The constituent of sweet and bitter almonds which, in contact with water and amygdalin, decomposes the latter (xv, 426).

Simon's statements on the occurrence of emulsin, or a substance capable of decomposing amygdalin, in the seeds of the poppy and of other plants (xv, 427), have not been confirmed by Ortloff.

Emulsin is not known in the separate state. See Liebig and Wöhler's preparation of a solution of emulsin (xv, 427).

Ortloff macerates the paste of sweet almonds with three times its weight of water for 5 to 7 days at 19° to 25°; filters the liquid, which has become sour and is covered with coagulated albumin; precipitates the filtrate with alcohol of 82 p. c.; washes the precipitate with alcohol; and dries it at a temperature below 37°. Emulsin thus prepared, when left under water for 24 hours and occasionally shaken, leaves a large quantity of phosphates of the earthy alkalis; the purified *emulsin may then be precipitated from the filtrate by alcohol.*

Bull leaves the aqueous extract of sweet almond paste to itself for 12 hours; separates the watery liquid from the supernatant cream; removes legumin by acetic acid; and precipitates the emulsin from the filtrate by addition of 2 vol. alcohol of 85 p. c. When exposed to the air after washing with alcohol, it absorbs moisture, and is converted into a brown transparent gum, which when triturated with water, dissolves but partially, and leaves a residue containing 20 to 44 p. c. of phosphates. After washing with ordinary and absolute alcohol in succession, and drying in a vacuum over oil of vitriol, it is obtained as a white lustreless friable mass, much more soluble than that which has been dried in contact with the air, but still yielding a considerable quantity of ash.

Thomson & Richardson leave almond-milk mixed with several times its volume of ether to stand for several weeks; then remove the ethereal layer; and precipitate the lower, nearly colourless aqueous liquid with alcohol. The precipitate obtained in the latter case no longer acts upon amygdalin; the precipitate formed by alcohol is, after drying in a vacuum, a white powder which dissolves in water. On the reaction of this emulsin with baryta, see below.

Robiquet's *synaptase* (*J. Pharm.* 24, 326; *Ann. Pharm.* 28, 389) is obtained by freeing the extract of almond paste from legumin by acetic acid, and from gum by neutral lead acetate; then removing the excess of lead from the filtrate by sulphuretted hydrogen; expelling the excess of that gas by leaving the filtrate in a vacuum; and finally precipitating with alcohol. It is yellowish-white, brittle, and shining, very soluble in cold water; the solution coagulates at 60°, and becomes turbid and fetid by exposure to the air. It is coloured rose-red, without precipitation, by iodine, and still acts on amygdalin, even at 80°. According to Ortloff and Bull, the precipitate formed by lead acetate decomposes amygdalin, but the filtrate does not.

Properties. Recently precipitated emulsin forms white flocks which dry up to a white lustreless mass (Bull). Ortloff's emulsin is a red-grey or red-yellow gum.— Scentless and tasteless. According to Bull, it has an acid reaction.

	Thomson & Richardson.	Bull. *at* 100°—130°.	Ortloff.
C	48·78	43·06	27·9
N	18·82	11·52	9·3
H	7·73	7·20	5·4
O and S	24·67	38·22	57·4
	100·00	100·00	100·0

Thomson & Richardson do not appear to have determined the amount of ash in their emulsin. Bull's emulsin contained 22 to 36 p. c. ash, Ortloff's 17·5 p. c., which are deducted.

Decompositions and Combinations. — Emulsin, after drying at 100° for some hours, is still capable of decomposing amygdalin; aqueous emulsin is coagulated by boiling, and then becomes inactive (xv, 426) (Bull).

Aqueous emulsin becomes turbid at 35° to 36°, opaque at 45°, and begins at 80° to deposit a granular precipitate, the quantity of which goes on increasing up to boiling heat. If the liquid be filtered after a few minutes' boiling (and after cooling? Kr.), the filtrate becomes opaque every time that it is heated, and clear again on cooling (Bull).

a. The granular precipitate, amounting to $\frac{1}{10}$ of the emulsin, is white, friable, and contains 48·74 to 59·1 p. c. phosphates of the earthy alkalis, besides nitrogenous organic matter in which plumbate of potash does not indicate the presence of sulphur. — *b.* From the filtrate alcohol throws down 30 p. c. of the emulsin, as a white granular precipitate containing 18 to 35 p.c. phosphates, and after deduction of these, 42·92 p. c. C., 6·87 H., 8·48 N., 41·73 S. and O. This precipitate dissolves in water, leaving only a small residue; and on adding lead-acetate to the solution, the sulphuretted portion is precipitated as a lead-salt, which, when decomposed by hydrosulphuric acid, yields a syrup containing nitrogen and phosphoric acid. There remains in solution a nitrogenous gum, which forms a jelly with potash. — *c.* After the precipitation with alcohol, a product of the decomposition of emulsin remains in solution, amounting to one-fourth of the emulsin used (Bull).

Aqueous emulsin decomposes, with turbidity and evolution of gas, when left exposed to the air for several days (Bull). The decomposition is not attended with evolution of sulphuretted hydrogen, and the power of the emulsin to act upon amygdalin is not completely destroyed till after several weeks (Ortloff). — By tincture of *iodine* aqueous emulsin is coloured rose-red according to Robiquet, not altered according to Ortloff, precipitated yellow-brown according to Bull.

Emulsin dissolves in fuming *hydrochloric acid*, without producing the blue coloration characteristic of the proteides. Aqueous emulsin is not precipitated by acids; acids prevent the coagulation of emulsin on boiling (Ortloff).

Emulsin swells up in potash-ley, with evolution of ammonia, but does not dissolve; it does not yield alkaline sulphide by boiling with potash (Ortloff). With boiling *baryta-water*, it continually gives off ammonia, and forms a soluble bitter baryta-salt, perhaps belonging to a peculiar acid, *emulsic acid* (Thomson & Richardson).

From aqueous emulsin, *alkaline carbonates* throw down white flocks soluble in excess; *baryta-water* and *lime-water* throw down jellies, which are insoluble in excess of the precipitant, but dissolve in nitric acid; most metallic salts and tannic acid throw down white precipitates (Ortloff).

When emulsin recently precipitated and redissolved in water is freed from phosphates by *lime-water*, the filtrate, which still, however, acts upon amygdalin, is not precipitated by neutral acetate of lead; but from the aqueous solution of the dried emulsin which has been precipitated by lime-water, neutral acetate of lead throws down large quantities of a lead-salt, by the decomposition of which with hydrosulphuric acid, a nitrogenous, acid, amorphous gum is obtained, which does not dissolve in alcohol or ether, and forms a soluble salt with magnesia, insoluble salts with baryta and silver oxide (Bull).

Emulsin is insoluble in *alcohol* and in *ether*. — Aqueous emulsin is precipitated by alcohol, merely in consequence of the presence of phosphates of the earthy alkalis. When almond-milk is neutralised with lime-water or ammonia, the filtrate is no longer precipitable by alcohol, but still acts upon amygdalin.

From aqueous *gummic acid* purified by dialysis, and from *albuminic acid* purified in like manner (p. 305), aqueous emulsin throws down white pulverulent precipitates soluble in acetic acid; impure albuminic acid and gum arabic are not precipitated (Graham, *Ann. Pharm*, 121, 62).

Diastase.

Payen & Persoz. *Ann. Chim. Phys.* 53, 73; *J. Chim. méd.* 9, 358; *Berzel. Jahresber.* 14, 281; *Ann. Chim. Phys.* 56, 337.

Payen. *Ann. Chim. Phys.* [4], 7, 387; *Jahresber.* 1866, 662.

Dubrunfaut. *Compt. rend.* 66, 274; *Les Mondes*, 16, 317; *Chem. Centr.* 1868, 1025.

Maltin of Dubrunfaut. — The constituent of germinating cereal-grains which effects the conversion of starch into dextrin and sugar. Discovered by Payen & Persoz in 1863.

Occurrence. Most abundantly in germinating cereal-seeds when the radicles have attained the length of the grain. Also in the eyes of potatoes, and in the parts below the buds of *Aylanthus glandulosa.* The radicles of cereal grains, the roots and full grown shoots of potatoes are free from diastase (Payen and Persoz). The radicles, but not the cotyledons of cereal-seeds, have the power of converting starch (Balling, *Gährungschemie*, 3 Aufl. 1, 1, 273).

Since paste prepared with river water liquefies on standing, which is not the case with paste prepared with boiled or distilled water— since further starch is liquefied by cold-prepared infusion of raw wheat or rye, or of raw barley at 50°, and tannic acid added to these liquids throws down active precipitates, whilst the filtrate becomes inactive, Dubrunfaut supposes them to contain diastase or a similar ferment. — The ptyalin of saliva (p. 347) is, according to Coutaret (*Compt. rend.* 70, 382; *Chem. Centr.* 1870, 18), identical with diastase.

Preparation. Fresh malt is triturated with half its weight of water, and the liquid strained and pressed from it is mixed with a quantity of alcohol sufficient to precipitate the greater part of the nitrogenous matter, then filtered, and the filtrate is precipitated with an additional quantity of alcohol. The impure diastase thus obtained is purified by dissolving it three times in water and precipitating with excess of alcohol, and dried in a stream of air at 45°—50° (Payen & Persoz).

More recently Payen (*Ann. Chim. Phys.* [4], 7, 387) uses only barley from the last harvest, and of one and the same variety, which has germinated regularly, is free from mould, and has formed sprouts equal in length to the grains. It is dried in a current of air at a temperature not exceeding 50°, freed from the radicles, coarsely ground, and digested for an hour or two with water of 30°. The solution separated by pressure and filtration is evaporated on the water-bath at a temperature not exceeding 70°—75°, filtered from the coagulated albumin, and precipitated by stirring it briskly with alcohol not anhydrous and not in excess.

Diastase thus prepared is, according to Dubrunfaut, a mixture containing the ferment of malt, Dubrunfaut's *maltin*, only partly in an altered state. From infusion of malt prepared at 40°, there are obtained: *a*, by heating to 75°; *b*, by precipitation with 2 or 3 vol. alcohol; and *c*, by precipitation with excess of alcohol: various precipitates, of which that thrown down by 2 to 3 vol. alcohol is capable of liquefying 200,000 times its weight of starch, and converting 10,000 times its weight of starch into sugar, whereas the other precipitates have little or no activity.

a. The first precipitate, which separates after two hours' heating to 75°, is inactive after washing, and contains 15 p. c. nitrogen. The filtrate becomes less active at the same time. — *b.* When infusion of malt is completely precipitated with alcohol, the precipitate has but little activity. dissolves partially in water, and contains 8 to 9 p. c. nitrogen. By solution in water and reprecipitation with alcohol, it is obtained poorer in nitrogen, and still less active, and then dissolves in water to a gummy strongly lævorotatory liquid. On repeating the solution and precipitation, the precipitate suffers still further diminution, both in quantity and in activity. — *c.* When infusion of malt is precipitated with 2 to 3 vol. alcohol of 90 p. c., flocks of maltin are precipitated, together with an insoluble substance rich in nitrogen. They exhibit the above-mentioned reaction with starch, and are strongly lævorotatory. — *d.* When the filtrate is mixed with more alcohol as long as a precipitate is thereby formed, an optically inactive syrup is thrown down, which is soluble in water, contains 3 to 4 p. c. nitrogen, and liquefies only 2,000 times its weight of starch (Dubrunfaut).

The diastase obtained by the process of Payen & Persoz is nearly white, amorphous, tasteless, and neutral to vegetable colours. It contains less nitrogen in proportion as it has been more completely purified.

On the action of diastase on starch, see xv, 90 and 306; further, Musculus (*Compt. rend.* 54, 194; *Jahresber.* 1861, 719; — *Ann. Chim. Phys.* [4], 6, 177; *Chem. Centr.* 1865, 1163; *Jahresber.* 1865, 598) and Payen (*Compt. rend.* 53, 1217; *Jahresber.* 1861, 717. — *Ann. Chim. Phys.* [4], 7, 387; *Jahresber.* 1866, 662), who maintain the correctness of their former views.

Mulder (*Chemie des Bieres*, Leipzig, 1858, 193), and Oudemans & Rauwenhoff (*Scheik. Onderz.* 2, 1, 1; *Jahresber.* 1858, 49) regard the independent existence of a peculiar organic compound possessing the power of converting starch into sugar, as not established.

Dry diastase, when *kept* for a long time, loses its power of converting starch; diastase dissolved in water quickly becomes acid, and at the same time inactive (Payen & Persoz). After two or three days keeping in moist air, it forms lactic acid from starch (Boutron & Frémy, *N. Ann. Chim. Phys.* 2, 257; *Ann. Pharm.* 39, 190.)—On the conditions under which the action of diastase on starch is arrested, see xv, 90.

Diastase does not act on the integuments of starch-granules, or on gum arabic, inulin, woody fibre, albumin, or gelatin. Its aqueous solution is not precipitated by *basic acetate of lead* (Payen & Persoz).

The action of diastase on starch is also prevented, according to Payen & Persoz, by *tannic acid.* According to Dubrunfaut, on the other hand, tannic acid throws down from infusion of malt, the salt which he designates as *tannate of maltin;* it contains 9 to 10 p. c. nitrogen, and 20 p. c. tannic acid, and acts upon starch like maltin.

The *cerealin* of Mège-Mourriès is a ferment-like body obtained from wheat-bran. The bran is freed from dextrin and sugar by six hours' digestion with 10 times its weight of dilute alcohol, then digested for half an hour with water, and the filtrate is evaporated at 40°.

The aqueous solution of this amorphous body coagulates at 75°; exhibits in a high degree the power of liquefying starch-paste, and induces lactic fermentation. It is not altered by rennet. Acids precipitate the cerealin in curdy flocks; alkalis do not render its solution perceptibly turbid, but they interfere with its power of liquefying starch-paste. Cerealin is insoluble in alcohol, ether, and oils (Mège-Mourriès, *Compt. rend.* 37, 351; 38, 505; 42, 1125; *Jahresb.* 1853 757; 1854, 332; 1856, 809).

Baregin.

Vauquelin. *Ann. Chim. Phys.* 39, 173.—*Ann. Chim. Phys.* 28, 98; *N. Tr.* 11, 1, 187.

Monheim. *Die Heilquellen von Aachen, Burtscheid, Spaa, Malmedy,* und *Heilstein.* Aachen, 1829, p. 238.

Gimbernat. *Repert.* 14, 270.—*Brugn. Giorn.* 12, 178.

Longchamps. *Ann. Chim. Phys.* 62, 144.

Daubeny. *Transactions of the Linnæan Society,* 16, 184; *Ann. Pharm.* 10, 336.

Bonjean. *N. J. Pharm.* 15, 321; *Pharm. Centr.* 1849, 856; *Jahresber.* 1849, 619.

Bouis. *Compt. rend.* 41, 1162.

Glairin of Chaptal; *Zoogen* of Gimbernat. A nitrogenous substance, occurring in many warm sulphur-springs, or formed in them under the influence of air and light. According to St. Vincent and Dutrochet, it is a plant, *Tremella thermalis* or *Nostoch thermalis;* Turpin, however (*Ann. Pharm.* 17, 344), found the nearly colourless, transparent, and gelatinous baregin of Longchamps to be perfectly destitute of organization, but to be filled with spores lying within it. Another kind of baregin, namely, that of Neris, is certainly organised. Such, indeed, is the distinction between the *barégine* and *sulphuraire* of Bouis.

The mineral water of *Vichy* flows out colourless, but, after standing for some time exposed to the air, becomes green by transmitted, red by reflected light, and deposits a brown glutinous sediment containing, besides lime, alumina, and ferric oxide, a nitrogenous substance soluble in alkalis, and precipitated with brown or blue colour by acids. The green water deposits at 81° a green coagulum, which turns yellow at 100°; acids precipitate from it greenish-blue, gelatinous flocks, which dissolve with purple-red colour in aqueous carbonate of potash, and are reprecipitated by acids. Alcohol also throws down from the green water dark green flocks, whilst the filtrate appears yellow, and leaves on evaporation brown animal matter, together with salts. When the green water is evaporated, baregin separates on its surface in brown films, and alcohol throws down from the filtrate a brown, glutinous, very sweet substance, soluble in water, and precipitable by tincture of galls; finally there remains in solution, together with salts, a substance precipitable by tincture of galls (Vauquelin).

The mineral springs of *Aachen*, *Burtscheid*, *Spaa*, *Malmedy*, and *Heilstein* yield a water which deposits flocks of baregin on boiling. This baregin is gummy and greyish-white in the moist state, translucent, like horn, when dry. It is nitrogenous; does not putrefy; dissolves slightly in cold, more freely in hot water, to which it imparts the smell and taste of weak flesh-broth. It is precipitated from concentrated aqueous solution by acids, and redissolved by an excess; dissolves easily in aqueous caustic potash, less easily in carbonate of potash. The aqueous solution precipitates basic lead acetate slightly and slowly, not mercuric chloride; gradually reduces auric chloride, and precipitates tincture of galls. Baregin is not soluble in alcohol or in ether (Monheim).

The *water of Aix in Savoy* smells like broth, in consequence of the presence of animal matter, and is precipitated by mercuric chloride and tincture of galls. The vapours which rise from the hot spring impart the same taste to water in which they are condensed; the water also becomes turbid and slimy, and deposits gelatinous flocks, which dry up to a nitrogenous, translucent film, putrefy in the moist state, dissolve in boiling water, and yield gelatin on evaporation. — Similar phenomena are exhibited by the hot springs of Baden and Ischia (Gimbernat).

Bonjean distinguishes glairin, glairidin, and zoïodin. *Glairin* from the sulphur-water of Aix is white-grey after drying at 40°, inodorous, and horny. It contains a little nitrogen but no iodine; dissolves slightly in water, more freely in concentrated acids, and is precipitated from this solution in blue-white flocks. — The water which drops from the glairin deposits Bonjean's *zoïodin* in violet laminæ; the water of Aix, mixed with rain-water, deposits *glairidin* (Bonjean).

Yeast.

THÉNARD. *Ann. Chim.* 46, 294; *N. Gehl.* 2, 408.
COLIN. *Ann. Chim. Phys.* 28, 128; 30, 42.
BRACONNOT. *Ann. Chim. Phys.* 47, 59.
QUEVENNE. *J. Pharm.* 24, 265, and 329; *J. pr. Chem.* 14, 328, and
MULDER. *Scheik. Onderzoek.* 2, 409; *Berzel. Jahresber.* 25, 720.
SCHLOSSBERGER. *Ann. Pharm.* 51, 193; *Berzel. Jahresber.* 25, 736.

R. Wagner. *J. pr. Chem.* 45, 241; *Lieb. Kopp Jahresber.* 1847 and 1848, 470.
Liebig. *Ann. Pharm.* 153, 1.

Beer-yeast. Wine-yeast. Ferment. — On the conditions of yeast-formation, the external properties of yeast, and its action on sugar, see xv, 265—276.

Yeast is a form of development of various kinds of fungus, and in the mature state consists, according to Lermer, of the cell-wall; the primordial sac adhering thereto; a granulo-mucous substance; the protoplasma; and a watery cellular liquid, which lies in the protoplasma in greater or lesser drops, the vacuoles.

The beer-yeast used for the following analyses was either thoroughly washed, or purified by the following process given by Schlossberger and Wagner.

The yeast contaminated with residues of beer and hops, is washed by stirring it with water, and leaving it to settle; the washed deposit is strained through fine linen which allows the yeast-cells to pass through, but retains the mechanical admixtures, and in this manner the portion of the yeast-substance insoluble in water is obtained. For analysis it is exhausted with cold and hot alcohol, and then with boiling ether, both of which liquids dissolve out resins, bitter substance, and fat, liquid and solid. After this treatment, and drying at 100°, the yeast appears as a white, scentless, and tasteless flour; the cells, which have become somewhat smaller, exhibit, instead of a nucleus, numerous small grains (Schlossberger).

Analyses of Yeast.

					Schlossberger.		Wagner.		Reichenbach.
	Marcet.	Dumas.	Mitscherlich.	Mulder.	*a.*	*b.*	*a.*	*b.*	*at* 100°.
C	30·5	50·6	47·0	50·85	49·52	47·58	44·37	49·76	34·57
N	7·6	15·0	10·0	11·08	12·14	9·89	9·20	9·17	7·41
H	4·5	7·3	6·6	7·16	6·61	6·47	6·04	6·80	

In Marcet's analysis, and, apparently, in that of Reichenbach (*Ann. Pharm.* 153, 10) the ash is not deducted.

Yeast contains sulphur as a constant constituent (Quevenne; Braconnot; Liebig); 0·6 p. c. S. (Mitscherlich); 0·387 to 0·685 p. c. (Liebig).

The composition of yeast varies from one day to another, in consequence of changes going on within it (Liebig). Wagner also found yeast merely washed with water and dried, to be very variable in composition. Schlossberger's top-yeast (*a*), after standing for a week at 10° in contact with a little beer, whereupon a considerable quantity of carbonic acid was evolved, contained only 9·14 p. c. nitrogen. — The amount of ash varies, on the average, from 7 to 8 p. c. (Liebig). Schlossberger's top-yeast (*a*), treated as above, contained 2·5, his bottom-yeast (*b*) 3·5 p. c. ash; Wagner's bottom-yeast (*b*) contained 5·29 p. c. ash. — On the composition of the ash, see Mitscherlich, Bull (*Pogg.* 76, 338), Liebig (*Ann. Pharm.* 153, 11).

Yeast-cells consist of a non-azotised membrane, and an internal substance containing both azotised and non-azotised constituents.

By alternate treatment with acetic or weak hydrochloric acid, and warm potash-ley, the *cell-membranes* are obtained translucent, not quite free from granular matter, not quite free from nitrogen, and to an amount not exceeding 17 p. c. of the dry yeast. They then contain, at 100°, after deduction of about 1 p. c. ash, 44·90 p. c. C., and 6·73 H.; produce grape-sugar when boiled with dilute sulphuric acid; do not dissolve in aqueous acids or in cuprate of ammonia (Schlossberger, Liebig). Mulder, by treating yeast with potash and hydrochloric acid, obtained the cellular substance of the membranes as a semi-transparent jelly containing 44·57 p. c. C. and 6·25 H.

Yeast-cells swell up under *water*, the vacuoles then increasing in size, till they sometimes extend to the cell-walls; at the same time water is taken up, and liquid from the contents of the cells passes into it (Lermer).

Even after repeated treatment with water, yeast still continues to give up organic matter to that liquid (Quevenne). Yeast-water leaves, on evaporation on a vacuum, a yellow-brown, bitter and acid residue, which dissolves slightly in water and ether, and is decomposed by water, with formation of a white deposit (Colin).

Water abstracts from yeast, proteides, phosphoric acid, acetic acid, lime, and dextrin, which bodies remain as a brown-yellow extract when the aqueous solution is evaporated. From yeast which has been exhausted with cold water, boiling water still extracts a large quantity of altered protein-substance, phosphoric acid, and lime; the deliquescent extract which remains on evaporation, yields, when its aqueous solution is precipitated with alcohol, a precipitate containing 39·59 p. c. ash, and in the organic part, 42·63 p. c. C., 12·68 N., and 6·59 H. (Mulder).

500 grammes of moist beer-yeast, washed on a filter with cold water, yield thereto less than 0·1 grm. phosphoric acid. But when 280 grammes of this washed yeast, corresponding to 48·2 grammes of yeast dried at 100°, are suspended at a time, in 1,600 cub. cent. of water containing creosote, de-aerated by boiling, and cooled to 40° in a stream of carbonic acid, and the liquid is left each time to itself for 24 hours at 20° to 30°, the quantity of phosphoric acid extracted by eight such washings amounts to 1·63 grm., or more than ¾ of the whole quantity present. The first four portions of water take up quantities of phosphoric acid, varying between 56 and 76 milligrammes; the fifth portion takes up 346; the sixth, 444; the seventh, 371; and finally, the eighth takes up 190 milligrammes of phosphoric acid. There remains a skeleton of yeast, which is still capable of inverting sugar and exciting fermentation (Béchamp, *Compt. rend.* 61, 689; *Par. Soc. Bull.* [2], 5, 396; *Jahresber.* 1865, 601).

When fresh pasty beer-yeast is washed by decantation four times in succession, with 6 to 8 vols. water, and then suspended in water, this last water takes up little from it in three or four hours; but if the yeast thus washed be placed for some time in contact with its own volume of water, it again gives up to the water a large quantity of organic matter, whereby a slightly acid, colourless, and tasteless liquid is obtained, which exhibits a slight milky turbidity with basic lead acetate and with tannic acid, and deposits white flocks in contact with the air. The liquid mixed with traces of prussic acid, remains clear, and free from mould for weeks. The liquid, whether containing prussic acid or free from it, brings about the conversion of cane sugar into inverted sugar, described at page 273, vol. xv, but loses this property by boiling. It contains the ferment precipitable by alcohol, mentioned at page 273, vol. xv. (Berthelot), Béchamp's *Zymase*. See Béchamp (*Compt. rend.* 59, 496; *Jahresber.* 1860, 574).

Yeast, when covered in the pasty state with water, gives off in the cold, and more abundantly when heated to 30°—35°, carbonic acid without nitrogen, and produces alcohol. At the same time the quantity of cellulose in the yeast (or at all events of a constituent insoluble in weak potash-ley and dilute hydrochloric acid) does not diminish in such quantity as to allow us to suppose that the alcohol results entirely from its decomposition (Liebig). Yeast-cells completely deprived of sugar by fermentation do not sprout any more; they possess thicker membranes, and the plasma contained in them is granular, and diminished in quantity (Nägele).

The liquid standing over fermented yeast, and obtained by washing out the residue, deposits coagulated albumin on boiling; it contains phosphoric acid, a nitrogenous and sulphuretted body precipitable as a syrup by alcohol, and leucine. Yeast-cells, exhausted by fermentation and washing, dry up to a brown tenacious mass, containing, on the average, 5·64 p. c. N., and 0·53 S., that is to say, a smaller proportion of nitrogenous constituents than fresh yeast. They yield to weak potash-ley a substance resembling casein, containing 11·39 p. c. N., and precipitable from alcoholic solution by acids (Liebig).

On suspending half a kilogramme of washed beer-yeast free from sugar, in water which has been de-aërated by boiling, mixed with a few drops of creosote and left to cool in a stream of carbonic acid, and digesting it for five days at 30°—50°, very pure nitrogen is evolved (see above), and 10 grammes of alcohol are produced (Béchamp, *Compt. rend.* 58, 601; *Jahresber.* 1854, 575). In the fermentation of sugar induced by press-yeast, there is formed, in addition to the bodies mentioned on page 275, vol. xv, a vegetable base, having the composition $C^{26}N^4H^{20}$ (Oser, *Wien. Acad. Ber.* 56, 489; *Chem. Centr.* 1869, 141).

Moist yeast when *kept*, first becomes sour, absorbs oxygen, and gives off carbonic acid (Thénard), and is then converted into an ammoniacal mass resembling old cheese (Proust). *Putrid* yeast contains crystals of ammonio-magnesian phosphate (Quevenne), tyrosine, butyric acid (A. Muller, *J. pr. Chem.* 57, 162, and 447), also trimethylamine and other amine-bases, various fatty acids, and pseudoleucine* (Hesse, *J. pr. Chem.* 71, 471.—*Ann. Pharm.* 119, 368). The incipient putrefaction is arrested by addition of sugar, and converted into fermentation (Schlossberger). Putrefying yeast produces nitrite of potash from the nitrate (Liebig).

Fresh beer-yeast eliminates a large quantity of oxygen from *peroxide of hydrogen*, and rapidly decomposes *persulphide of hydrogen*; it loses this faculty by boiling (Schlossberger).—In its decomposition by *nitric acid*, nitrogen, carbonic acid, and nitric acid are given off, and a tallow-like substance is formed (Thénard). *Nitric acid* in contact with yeast gives off gas-bubbles and an odour of formic acid, and turns yellow. The yeast, which has turned yellow at the same time, gives up xanthoproteic acid to ammonia, after washing, whilst the cell-membranes remain behind, still coloured yellow (Mulder). — *Chlorine gas* passed into water in which yeast is suspended, forms a brown mass: Mulder's protein-chlorous acid (p. 265), which is separated by ammonia into a portion which dissolves, and insoluble cellular substance (Mulder). — *Oil of vitriol* forms a cherry-red, *hydrochloric* acid, a violet solution (Quevenne). *Hydrochloric acid* abstracts albuminous matter, and on application of heat, produces ammonia and brown products of decomposition (Mulder).

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* This pseudoleucine is a sulphuretted body, apparently identical with the peculiar substance found by Bopp in the mother-liquor of leucine (xii, 427, 2). It is likewise obtained from horn, from the neck-band of the ox, from blood-fibrin, syntonin, albumin, and casein; it is a mixture containing leucimide or leuconitrile, $C^{12}NH^{11}O^2$, and yielding that compound by sublimation (Hesse, *loc. cit.*; Erlenmeyer, *Ann. Pharm.* 119, 117; *Jahresb.* 1861, 778).

Ammonia attacks yeast slightly, and, according to Mulder, dissolves out of it a small quantity of protein-substance. — Moderately strong *potash-ley* at the boiling heat, dissolves yeast completely, forming a brown liquid, with evolution of ammonia (Thénard); also forming sulphide of potassium (Quevenne).

Yeast treated by Schlossberger's method, yields to very dilute potash, with evolution of ammonia, a protein-substance, which is thrown down by acids in white flocks, and re-dissolved by excess of acetic acid. After drying at 100°, it contains 55·08 p. c. C., 13·88 N., 7·5 H., acquires a fine violet colour when treated with strong hydrochloric acid, and is precipitated from its acetic acid solution by ferrocyanide of potassium.—The filtrate from these flocks contains a small quantity of yellow-brown extract (Schlossberger).

From wine-yeast, aqueous *carbonate* of potash extracts animal substances, which are precipitated from the gummy solution by acetic acid. It is not soluble in acids; dissolves very easily in alkaline water; completely in lime-water, from which it is precipitated by carbonic acid; carbonate of lime and carbonate of magnesia produced partial dissolution. It diffuses itself uniformly in water, and when the liquid is heated, collects into flocks, which have become insoluble in alkalis and in lime-water (Braconnot).

Acetic acid does not cause yeast to swell up (Quevenne), but extracts from it a protein-substance, without altering the cell-membrane (Schlossberger). The protein-substance precipitated from the acetic solution by carbonate of ammonia, contains at 130°, 53·55 p. c. C., 16·03 N., 7·04 H., 0·25 S., and 22·23 O., neither phosphorus nor ash (Mulder). — Cold *alcohol* in contact with yeast, acquires a fine yellow colour (Quevenne); boiling alcohol extracts a small quantity of fat, but no vegetable gelatin (Mulder). The extracts obtained by successive treatment with cold alcohol, boiling alcohol, and *ether*, contain nitrogenous substances, a semifluid fat, phosphoric acid, lactic acid, and other matters (Quevenne). The ethereal extract of wine-yeast contains cholesterin and a nitrogenous and phosphoretted body, perhaps lecithine (p. 374) (Hoppe-Seyler).

For the completion of these statements, and of those made in vol. xv, p. 265, *et seq*, respecting fermentation and yeast, see the following memoirs:—

On Fermentation in general:—LEMAIRE (*Compt. rend.* 57, 958; *Jahresber.* 1863, 382); BÉCHAMP (*Compt. rend.* 56, 1232, 57, 677; *Jahresber.* 1863, 584. — *Compt. rend.* 58, 601, and 1116; *Jahresber.* 1864, 575, and 577); PASTEUR against BÉCHAMP (*Compt. rend.* 57, 967); BERTHELOT against BÉCHAMP (*Compt. reed.* 58, 723).—On Lactous

Fermentation, and the Fermentative Action of Chalk therein: **Béchamp** (*Compt. rend.* 63, 451; *Jahresber.* 1866, 668).

On the Derivation, Origin, and Propagation of Yeast: **Joly** & **Musset** (*Compt. rend.* 53, 368; *Jahresber.* 1861, 725); **Pasteur** (*Bull. Soc. Chim.* 1862, 66; *Jahresber.* 1862, 473); H. **Hoffmann** (*Compt. rend.* 60, 633; *Jahresber.* 1865, 602). — Behaviour of Yeast when heated: H. **Hoffmann** (*Compt. rend.* 63, 929; *Jahresber.* 1866, 668). — Influence of Pressure and Cold on Yeast: **Melsens** (*Compt. rend* 70, 629). — Influence of Addition and Abstraction of Water: **Wiesner** (*Wien. Akad. Ber.* 59 (2, Abth.) 495; *Chem. Centr.* 1870, 191).

On a peculiar Ferment, occurring only in summer, which converts cane-sugar into Parasaccharose: **Jodin** (*Compt. rend.* 53, 1252; *Jahresber.* 1861, 722. — *Compt. rend.* 55, 720; *Jahresber.* 1862, 472. — *Compt. rend.* 57, 434; *Jahresber.* 1864, 572).

On the Presence of Ammonia in Carbonic Acid produced by Fermentation: **Millon** (*Compt. rend.* 57, 235; *Jahresber.* 1863, 583. — *Compt. rend.* 59, 144; *Jahresber.* 1864, 579). — **Duclaux** (*Compt. rend.* 58, 1114; 59, 450; *Jahresber.* 1864, 578).

On Fermentation in general: **Liebig** (*Ann. Pharm.* 153, 1 and 137). **Raulin** (*Compt. rend.* 70, 634).

On Alcoholic Fermentation, and the Mode of Nutrition of the Yeast-plant: **Ad. Mayer** (*Pogg.* 153, 293; *Chem. Soc. J.* [2], 9, 426).

ADDENDA.

To page 281.

Paralbumin.

P. Plösz. *Med.-chem. Unters.* 1871, 517.

Hoppe-Seyler (*Chem. Centralbl.* 1862, No. 56) found that the paralbumin which Scherer obtained from ovarian cysts, &c., contains besides albumin, a body which, like glycogen (xv, 183), dissolves in water with milky opalescence, is insoluble in alcohol, is turned brown by alkalis and yellow by iodine, and when boiled with dilute sulphuric acid, reduces cupric oxide and bismuth oxide.

Paralbumin is therefore a mixture containing albuminous substances and a reducing substance. The albumin is held in solution by alkali, from which it is precipitated by a larger quantity of water and by carbonic acid, or by very dilute acetic acid. By alcohol it is precipitated together with a portion of the alkali; and after long standing under alcohol, it is redissolved by moderately warm water. On boiling a cystic fluid, a portion of the albumin is coagulated; but if the liquid be neutralised before boiling, the whole of the albumin is coagulated. Dilute hydrochloric and sulphuric acids convert it into syntonin, which can then be precipitated by sodium sulphate or chloride. The reducing body remains in solution when either method of precipitation is employed, and may thus be easily separated from albuminous matters:

α. The liquid is carefully neutralised with dilute acetic acid, and precipitated with thrice its volume of alcohol. The precipitate is washed with alcohol on a filter, pressed, mixed with water, and heated to the boiling point; and the solution filtered from the coagulated albumin is kept exactly neutral, concentrated to a small bulk, and precipitated with alcohol. The precipitate, after being well washed with water, contains the substance free from albumin. To purify it still further, it is again dissolved in water, heated to the boiling point, filtered, and again precipitated and washed with alcohol.

β. Another cystic fluid was mixed with an equal volume of a saturated solution of sodium chloride and so much hydrochloric acid that one grm. HCl was contained in 100 c.c. In this manner the albuminous body was very completely precipitated, after being changed into syntonin. The liquid was separated from the precipitate by straining and filtration, lastly neutralised, and evaporated to a small bulk, then filtered from the sodium chloride, which had separated, and from some albumin; next precipitated by a large quantity of alcohol, and washed.

Lastly, the substance was redissolved in water, warmed, filtered, and reprecipitated by alcohol.

The reducing substance thus prepared contains a considerable quantity of sodium chloride, from which it can be freed only by prolonged washing with alcohol. By the other method, however, of precipitating the albuminous body by alcohol and heat, the liquid is separated from the precipitate with difficulty, and decomposition may ensue from prolonged contact with water.

The substance thus obtained is, when moist, white, gelatinous, and very like syntonin. It is soluble in water, and separates therefrom on concentration, in the form of a film, which, when dried, is of a dirty grey colour, like a dried brittle mass of albumin. When once dried, it no longer dissolves to form a clear solution. Its aqueous solution is opalescent, but can be rendered transparent by repeated filtration; but it again becomes turbid on standing. The body is precipitated from its solution by alcohol, mercuric chloride, and mercuric nitrate; but not by acids, either strong or dilute, by cupric sulphate, or potassic ferrocyanide. The aqueous solution dissolves cupric hydrate on boiling, without the addition of an acid, but does not reduce the oxide. It is not coloured by iodine.

On boiling its clear solution with mineral acids, a flocculent, dirty brown precipitate is produced. On filtering off this precipitate, the filtrate, after neutralisation, is no longer precipitable by alcohol; it reduces cupric hydrate in alkaline solution, before the boiling point is reached; bismuth oxide and indigo on boiling; and is turned brown when boiled with caustic potash. In aqueous solution this substance is decomposed by heating, as well as when boiled with acids, and then yields to alcohol considerable quantities of the reducing body.

The precipitate formed by this decomposition is insoluble in water, alcohol and acids, soluble in alkalis. It gives none of the reactions for albumin (formation of xanthoproteic acid on heating with strong nitric acid, violet coloration with cupric oxide, &c.).

Neither before nor after heating does the watery solution of the body exhibit any action on polarized light. The aqueous solution of the product of decomposition acts as a most energetic reducing agent, even when extremely dilute.

The original substance gave by analysis 49·7 p. c. carbon, 7·4 to 8·8 nitrogen, and 7·6 hydrogen. The variable percentage of nitrogen is accounted for by the readiness with which the body is decomposed; and hence the varying quantities of the reducing body which it contains. This latter is probably a kind of sugar, and consequently the original substance is a glucoside; it bears considerable resemblance to some of the varieties of mucin (p. 347).

The reducing body, in its original state, previous to boiling with acids, dissolves in cold strong nitric acid, and the solution yields with water a finely flocculent, light yellow precipitate, consisting of a nitrate. The compound thus formed appears to be different from that which is obtained by heating albuminous bodies with nitric acid; it is still precipitable after being heated for a short time with water, but dissolves as the acid is washed out. The nitric acid compound does not explode by heat or by percussion.

To page 347.

Mucin from the Submaxillary Gland.

J. Obolensky. *Med.-chem. Unters.* 1871, 590.

The submaxillary glands of an oxen, after being well washed, are triturated with pounded glass; the mass is thrown into water, and left over night; the liquid filtered; the residue again treated in the same manner; the filtrates precipitated with excess of acetic acid; the precipitate washed continuously first with water and a little acetic acid (till the filtrate was no longer clouded by ferrocyanide of potassium), then with hot alcohol; and the remaining substance is dried. It is only the submaxillary gland that yields a body insoluble in acetic acid; the parotid gland yields to water nothing but proteids (globulin).

Mucin thus prepared yields 2·44 p. c. ash containing 1·07 p. c. phosphoric acid. The organic substance contains neither sulphur nor phosphorus, and yields by analysis—

C	52·31	52·08
N	11·81	11·90
H	7·22	7·14
O	28·63	28·88

These numbers agree nearly (excepting in the nitrogen) with those which Scherer obtained by the analysis of mucin from a cystic fluid (p. 341), but differ considerably from that obtained by Eichwald (*ibid.*).

Submaxillary mucin recently precipitated and still moist, swells up considerably in water, dissolves easily in lime- and baryta-water, and is not precipitated therefrom by tannic acid, ferric chloride, or mercuric chloride. The solution of mucin in soda-ley forms with cupric sulphate a blue solution, which turns reddish when boiled, without separation of cuprous oxide. It is quite insoluble in acetic acid, soluble in strong hydrochloric or nitric acid. The hydrochloric solution soon turns blue; the nitric solution yellowish, without yielding an orange colour with soda-ley. The hydrochloric solution is precipitated by acetate of soda, not by water. Moist mucin dissolves in aqueous carbonate of soda, but not in hydrochloric acid of 10 p. c.

After treatment with hot alcohol, and drying over the water-bath, the mucin scarcely swells up in water, and dissolves but slowly in lime- or baryta-water, or in aqueous carbonate of soda. Its solution in caustic soda is precipitated by hydrochloric or nitric acid, very slowly by alcohol. The solution in lime- or baryta-water reacts with tannin, ferric chloride, and mercuric chloride in the same manner as the fresh mucin. It is not dissolved by aqueous chloride of sodium, either when saturated or when diluted with 3 vol. water. It dissolves in strong hydrochloric acid, the solution, like that of the fresh mucin, does not give a precipitate with ferrocyanide of potassium.

When dried and pulverised mucin is heated over a boiling water-bath with very dilute sulphuric acid, the resulting solution, even after 25 minutes' boiling—although a large portion of the substance still remains undissolved—and still more after 30 minutes, forms, when boiled with excess of soda-ley and a little cupric sulphate, a precipitate of cuprous oxide. When warmed with excess of soda-ley alone, the liquid turns brown; it likewise reduces bismuth oxide in alkaline solution, as well as sulphindigotic acid. If, on the other hand, the heating of the mucin with dilute sulphuric acid be continued for a longer time, the quantity of the reducing substance which passes into solution decreases, and appears ultimately to disappear altogether. This reducing substance is not dissolved by ether when its acid solution is agitated therewith; it is also insoluble in absolute alcohol, and is, therefore, different from grape-sugar and milk-sugar, from which it is likewise distinguished by its property of disappearing on prolonged heating with very dilute sulphuric acid.

Nuclein.

F. MIESCHER. Ueber die Chemische Zusammensetzung der Eiterzellen. *Med.-chem. Untersuch.* 1871, 441.—Die Kerngebilde im Dotter des Hühnereies, *ibid.* 502.

HOPPE-SEYLER. Ueber die Chemische Zusammensetzung der Eiters. *Med.-chem. Untersuch.* 1871, 486.

A substance resembling mucin, existing in pus-corpuscles and in the nuclear structures of the yolk of the hen's egg.

A. *From Pus-corpuscles.*—To obtain pus-corpuscles free from serum, the pus and articles soaked with it, such as surgical bandages, are treated with a mixture of 1 part saturated solution of sulphate of soda and 9 parts water, or, if the alkalies of the ash have to be estimated, with a saturated solution of nitrate of baryta diluted to one-half. In these liquids the pus-corpuscles sink to the bottom, and, after repeated washing; are obtained sufficiently pure, while the supernatant fluid is tolerably free from turbidity.

To isolate the nuclei, the corpuscles, after being treated in the cold with dilute hydrochloric acid, are shaken with a mixture of ether and water, whereupon the nuclei settle to the bottom of the watery liquid in the form of a fine powder.

Another method of isolating nuclei is to digest the pus corpuscles, after previous digestion in warm alcohol, in a pepsin solution made from an extract of pig's stomach, and containing 1 per cent. strong hydrochloric acid. The nuclei then remain, while the rest of the corpuscle is digested away; they resemble those obtained by the former method, except that they are more shrivelled and granular.

The nuclei consist of a substance soluble in dilute soda-solution, and another insoluble: *soluble* and *insoluble nuclein.* They are entirely soluble in strong hydrochloric acid and caustic alkalis

The substance of the nuclei contains nitrogen and sulphur, and is very rich in phosphorus, which is a real organic constituent.

Nuclein appears to be a definite chemical substance, and not a mere mixture (Miescher).

Pus-corpuscles are composed chiefly of albuminoids. When treated with a solution of sodium chloride of 3—10 per cent, they are converted into a gelatinous viscous mass. This depends, as Rovida has shown, on the formation of a ring of hyaline substance round each cell.

The constituent albuminoids appear to be—

1. Alkali-albuminate, partially precipitated by carbonic acid, more completely by acetic acid, insoluble in chloride of sodium, soluble in hydrochloric acid of 0·1 p. c. 2. An albuminoïd coagulable at 48°—49°, and consisting of flocculi insoluble in hydrochloric acid of 0·1 p. c., in sodium chloride, and in very dilute soda-solution. It is therefore not merely albumin dissolved in a phosphate. 3. An albuminoid coagulable at the ordinary temperature of serum albumin. In addition to these 4. Rovida's hyaline substance, a proteide insoluble in water, soluble in hydrochloric acid of 0·1 p. c., swelling up in salt water.

By treating the corpuscles with strong alcohol at 50°—60°, an extract is obtained, the greater part of which is soluble in ether, and contains lecithine, amounting to 41·3 p. c. of the whole extract, or 17·8 p. c. of the dry pus-corpuscles. This is not far different from the amount found by Parkes in the yolk of egg (protagon 52 p. c. = 20·7 p. c. lecithine). — The portion insoluble in ether yielded, when treated with sulphuric acid, a substance which gave the sugar reaction: probably cerebrin or a similar body — 100 pts of the dry corpuscles yielded 1·269 p. c. ash, containing 0·143 NaCl, 0·263 NaO, 0·655 KO, 0·083 CaO, 0·087 MgO, and 0·039 Fe^2O^3.

B. *From the yolk of the Hen's Egg.* — The yolk consists of yellow and white elements, the yellow constituting the principal part, the white being found chiefly under the yolk-membrane, round the germinal vesicle, and in a process extending from this into the centre of the yolk. The white yolk-elements differ much in size and appearance; they possess distinct cell-membranes and homogeneous contents, and within this is found a peculiar spheroïdal, solid, strongly refractive body. Sometimes more than one, and sometimes a great number exist, varying in size down to molecular fineness.

To determine the nature of these elements, the yolk was freed from membrane as far as possible, exhausted with ether, and then treated with boiling alcohol four times in four successive hours. The residue was boiled with water to get rid of the alcohol, and then subjected to digestion with pepsin. As an indigestible residue, a powdery white deposit remained, while the supernatant fluid remained clear. This deposit was washed till all turbidity with tannin ceased, then exhausted with warm alcohol and ether in order to get rid of any traces of lecithine or hystolytic products which might have been produced by the process of digestion.

The deposit thus treated consists chiefly of flakes or conglomerations of granules of various shapes and sizes, which are the peculiar nuclear bodies of the yolk-elements. Some of these have the same appearance as in the fresh yolk; others are variously changed, in consequence of the extraction of certain of their constituents. These nuclei are soluble in a 1 per cent. solution of sodium carbonate, forming a more or less opalescent liquid which contains no structural element, excepting a few fat globules. The solution is precipitated by acetic acid and by dilute hydrochloric acid, just like the solution of pus nuclei.

The precipitate gives the xanthoprotein reaction, a violet colour with potash and sulphate of copper, and a faint red with Millon's reagent. In other respects also it agrees with pus-nuclein. Alcohol dissolves a small portion, so likewise does ether.

The dry substance yields phosphorus in large quantity: in one case 0·3583 grm. nuclei gave 15·35 p. c.; in another, 0·2985 grm. nuclei gave 16·23 p. c. phosphoric acid. In the first case the nuclei were obtained from a soda-solution by precipitation with acetic acid; in the second by digestion.

When the substance is carefully heated till all ammoniacal vapours have disappeared, a bulky coke is left which, with the exception of ·5·03 per cent. phosphoric acid and a trace of silica, gives no ash.

The quantity of phosphorus obtained in this way is only one-third the whole quantity contained in the substance, the rest having disappeared. This indicates a peculiar organic combination of the phosphorus: a phosphoretted albuminoid substance, like the nuclein of pus.

One egg-yolk weighing about 15—20 grms., yields from 0·2—0·5 grm. dry nuclein. Hence of 15 per cent. albuminoid substance contained in the yolk, 1—1·5 per cent. at least is nuclein—a relation of nuclein to protoplasm which is higher than in the pus corpuscle. As the white yolk-elements are small in quantity as compared with the yellow, it follows that the yellow are also nucleated structures.

END.

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